THE PROCEEDINGS OF THE PHYSICAL SOCIETY

Vol. 43, Part 5 September 1, 1931 No. 240

CONTENTS

PAGE

Prof. J. E. Lennard-Jones. Cohesion . 461

Prof. S. Chapman. The Absorption and Dissociative or Ionizing Effect of Monochromatic Radiation in an Atmosphere on a Rotating Earth. Part II. Grazing Incidence 483

Messrs G. I. Finch, R. W. Sutton and A. E. Tooke. A Time Base for the Cathode-ray Oscillography of Irregularly Recurring Phenomena . . 502

Mr S. Zeidenfeld. The Hilger X-ray Crystallograph and the Cubic-crystal Analyser 512

Dr H. C. Hepburn. Electro-endosmosis and Electrolytic Water-transport. Part II . 524

Mr J. S. Badami. The Spectra of Trebly and Quadruply Ionized Antimony, Sb IV and Sb V 538

Mr S. Tolansky. The High-frequency Spectrum of Mercury and the Fine Structures of $\lambda 6123$ (Hg I) and $\lambda 4747$ (Hg II) 545

Mr Thomas E. Nevin. The Spectrum of Barium Fluoride in the Extreme Red and Near Infra-red 554

Dr H. Lowery and Mr T. S. Hartley. The Refraction and Dispersion of Gaseous Pentane and Chloroform . . . 559

PAGE

Dr H. Lowery and Mr J. K. Elliot. The Refraction and Dispersion of Gaseous Ethyl Bromide 562

Mr Albert Campbell. Two Precision Condenser Bridges 564

Dr W. N. Bond. Magnetostriction and Hysteresis 569

Dr H. R. Lang. On the Measurement of the Total Heat of a Liquid by the Continuous Mixture Method . . . 572

Mr C. R. Ensor. The Determination of Thermal Conductivity and its Temperature-variation for Medium Conductors 581

Dr R. L. Smith-Rose and J. S. McPetrie. The Attenuation of Ultra-short Radio Waves due to the Resistance of the Earth 592

Presentation of the Duddell Medal to Sir John Ambrose Fleming . . . 613

Obituary Notices:

Prof. H. L. Callendar 620

Prof. A. A. Michelson . . . 625

Mr H. Tomlinson 633

Reviews of Books 635

Index to Vol. 43 639

Price to Non-Fellows 7/- net; post free 7/3

Annual Subscription 35/- post free, payable in advance

Published by
THE PHYSICAL SOCIETY
1 Lowther Gardens, Exhibition Road
London, S.W.7

Printed by
THE UNIVERSITY PRESS, CAMBRIDGE

THE PHYSICAL SOCIETY

1931–32: OFFICERS OF THE SOCIETY

President:—Prof. Sir A. S. Eddington, M.A., D.Sc., F.R.S.

Hon. Secretaries:

Ezer Griffiths, D.Sc., F.R.S. (*Business*).

A. Ferguson, M.A., D.Sc. (*Papers*), 70 *Hadham Road, Bishops Stortford, Herts.*

Hon. Foreign Secretary:—Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

Hon. Treasurer:—R. S. Whipple.

Hon. Librarian:—J. H. Brinkworth, D.Sc., A.R.C.S.

Assistant Secretary:—J. J. Hedges, Ph.D., F.Inst.P.

Office of the Society:—1 *Lowther Gardens, Exhibition Road, London, S.W. 7.*

Editor:—Capt. C. W. Hume, M.C., B.Sc.,
14 *The Hawthorns, Finchley, N. 3.*

All communications, other than those to the Papers Secretary or the Editor, should be sent to the office of the Society, viz. 1 Lowther Gardens, Exhibition Road, London, S.W. 7

INSTRUCTIONS TO AUTHORS

Note. The acceptance of a paper for publication in the Proceedings rests with the Council, advised by its Editing Committee. The high cost of printing renders it imperative to exclude matter that is not novel and not of importance to the understanding of the paper.

Authors offering original contributions for publication in the Proceedings should observe the following directions; failure to comply with these may cause considerable delay in publication. Fuller directions, including special instructions on the arrangement of mathematical work, are contained in a leaflet obtainable from the Assistant Secretary.

Manuscript.—A clear and concise style should be adopted, and the utmost brevity consistent with effective presentation of the original subject-matter should be used. The copy should be easily legible, preferably typewritten and double-spaced. It should receive a careful final revision before communication, since alterations are costly when once the type has been set up. Mathematical expressions should be set out clearly, in the simplest possible notation.

References.—In references to published papers the author's initials and name followed by the title of the journal in italics, volume, page and year should be given thus: *Proc. Phys. Soc.* 43, 199 (1931).

Drawings and tables.—Diagrams must be carefully drawn in Indian ink on white paper or card. Their size and thickness of line must be sufficient to allow of reduction. *Lettering and numbering should be in pencil*, to allow of printing in a uniform style. The number of diagrams should be kept down to the minimum. Data should in general be presented in the form of either curves or tables, but not both. Footlines descriptive of figures, and headlines indicative of contents of tables, should be supplied.

Abstracts.—Every paper must be accompanied by an abstract in duplicate, brief but sufficient to indicate the scope of the paper and to summarize all novel results.

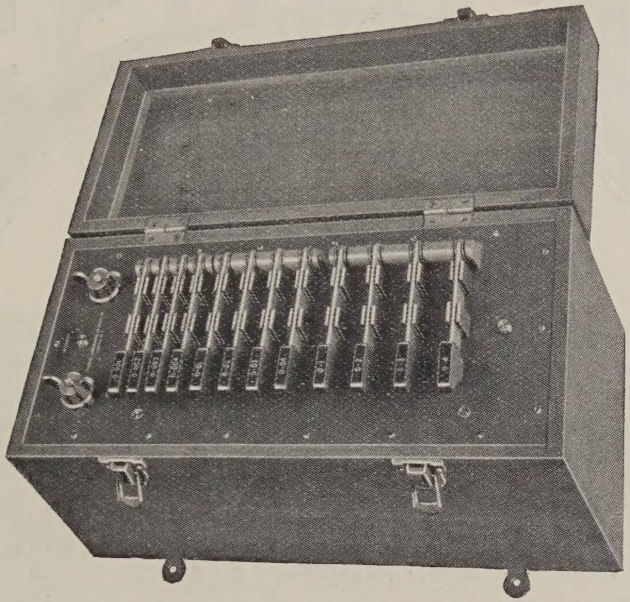
Proofs.—Proofs of accepted papers will be forwarded to authors. They should be returned promptly with errors corrected, but additions to or other deviations from the original copy should be avoided.

Reprints.—Fifty copies of printed papers will be supplied gratis. Extra copies may be purchased at cost price.

Contributions by non-Fellows.—Papers by non-Fellows must be communicated to the Society through a Fellow.

Republication.—Permission to reproduce papers or illustrations contained therein may be granted by the Council on application to the Hon. Secretaries.

DUBILIER
PRODUCTS



DUBILIER ADJUSTABLE
MICA-DIELECTRIC CONDENSERS

SUB-STANDARD TYPE

Adjustable in Steps of 0·001 μF. Max. Capacity 1·11 μF.

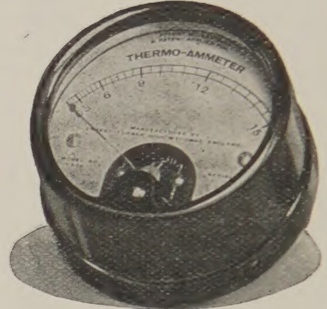
PRICE £27 · 0 · 0

This condenser is specially designed for use as a laboratory or works sub-standard for general testing purposes and bridge work. It can be constructed with a capacity tolerance of ±0·1%, and has a very low power factor.

Condensers of other ranges and capacity standards fitted with decade type switches can also be supplied. Prices on application.

DUBILIER CONDENSER CO. (1925) LTD
Ducon Works, Victoria Road, N. Acton, London, W. 3

TURNER



SIGNIFIES
ACCURACY, RELIABILITY & EFFICIENCY,
AND FIRST-CLASS
WORKMANSHIP & APPEARANCE
IN
ELECTRICAL
MEASURING
INSTRUMENTS.

MADE IN ENGLAND

Telephone:
HIGH WYCOMBE
301.

Telegrams:
"GORGEOUS,
HIGH WYCOMBE."

ERNEST TURNER,
CHILTERN WORKS,
55/73, TOTTERIDGE AVENUE,
HIGH WYCOMBE,
BUCKS.

Sole Agents in Australia & New Zealand:
AMALGAMATED WIRELESS (AUST.) LTD.
47, YORK ST, SYDNEY.

Sole Agents for Holland & Belgium.
KIPP & ZONEN,
DELFT, HOLLAND.

Chemical Resistance

plus Strength, Beauty and Economy

Several different materials may have equal resistance to chemical action, but one may lack physical strength, another dielectric strength, and a third be excessively difficult or costly to fabricate. An ideal material is one which combines all essential factors and properties. In Bakelite Materials chemical resistance is supplemented by many other valuable characteristics.

The maker of a small ozonizer uses Bakelite Moulding Material because be found it would resist ozone, and provide a more attractive device. A similar problem of ozone resistance, complicated by the need for electrical insulating properties, was solved by the use of Bakelite Laminated on the controller switches of a large water ozonizer.

In the case of a small sterilizer, the housing had to withstand frequent exposure to wet steam and formaldehyde fumes, and here, too, Bakelite Moulding Material was successfully used. Another instance is provided by the box for the instruments and chemicals required in dentistry, where Bakelite Mouldings are used because they are chemically resistant, non-staining, strong and disinfectant.

BAKELITE ENGINEERING SERVICE

Twenty-one years of experience in the development and manufacture of Bakelite Synthetic Resin Products enables Bakelite Limited to offer the co-operation of their Engineers and Laboratories in investigating the possibilities of these products for new applications

BAKELITE LIMITED

68 Victoria Street, London, S.W.1

Works: BIRMINGHAM (Est. 1910) and DARLEY DALE (Est. 1921)

Telephone: VICTORIA 5441 (4 lines)

BAKELITE

Registered B Trade Marks

TREFOIL

PHOTO-ELECTRIC CELLS
AND THEIR APPLICATIONS

A DISCUSSION ON THE HISTORY, DEVELOPMENT AND MANUFACTURE OF PHOTO-ELECTRIC CELLS, AT A JOINT MEETING OF THE PHYSICAL AND OPTICAL SOCIETIES

Editor—JOHN S. ANDERSON, M.A., D.Sc., F.Inst.P.

Containing Papers on the Theory, Manufacture, Properties and Applications of Photo-Electric and Selenium Cells, contributed by H. S. Allen, W. R. G. Atkins, E. A. Baker, N. R. Campbell, Theodore W. Case, L. J. Davies, G. M. B. Dobson, Heinrich Geffcken, K. S. Gibson, Harry D. Griffith, T. H. Harrison, A. S. G. Hill, Peter Paul Koch, Jakob Kunz, Donald H. Loughridge, Fritz Michelssen, Eric B. Moss, D. S. Perfect, C. E. S. Phillips, H. H. Poole, J. H. J. Poole, Hans Richter, H. R. Ruff, Fritz Schroter, P. Selenyi, Clayton H. Sharp, V. E. Shealford, L. G. Stoodley, H. Thirring, H. A. Thomas, N. L. Yates-Fish, together with a Report of the Discussion thereon.

236 *pages, with numerous illustrations*

PUBLISHED BY

THE PHYSICAL AND OPTICAL SOCIETIES

I LOWTHER GARDENS, EXHIBITION ROAD, SOUTH KENSINGTON, LONDON, S.W.7

PRICE 12s. 6d. POSTAGE EXTRA

BOOKS BOUGHT & SOLD

We are always glad to receive offers of second-hand Books and Journals, for which we are prepared to offer fair market prices and to pay cash; particularly complete sets or long runs of the following:

American Journal of Mathematics
Annali di Matematica
Astrophysical Journal
Faraday Society. Transactions
Fortschritte der Physik
Journal de Mathématiques
Journal de Physique
Journal für Mathematik. Crelle
Journal (Quarterly) of Mathematics
London Mathematical Society. Proceedings
Messenger of Mathematics
Philosophical Magazine
PHYSICAL SOCIETY. PROCEEDINGS
Physikalische Zeitschrift
Royal Society. Philosophical Transactions
Royal Society. Proceedings
Science Abstracts
Zeitschrift für Physik

And many other Scientific Journals

We shall also be glad to have enquiries for both new and second-hand books, of which we carry an immense stock. Librarians supplied with English and Foreign books. Librarians are invited to send us their lists of books wanted. Catalogue 340, Scientific Books and Publications of Learned Societies, sent post free on application.

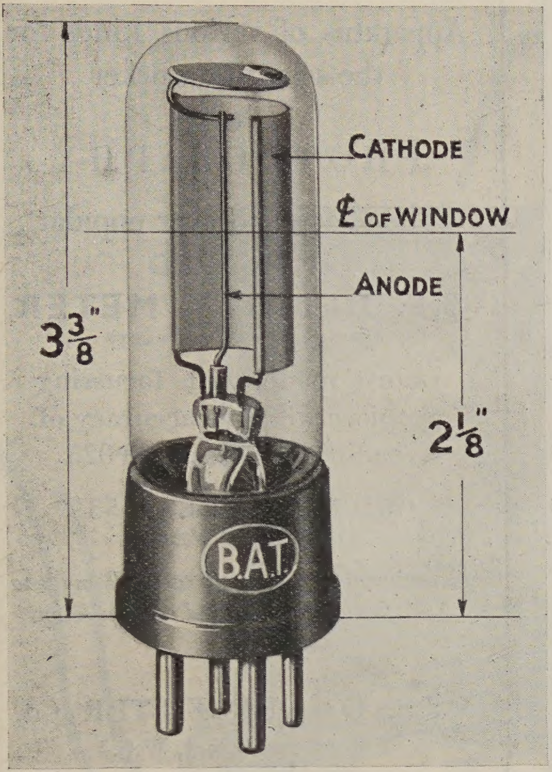
HEFFER'S BOOKSHOP

KNOWN ALL OVER THE WORLD & AS NEAR AS THE NEAREST POST-BOX
FOR BUYING & SELLING BOOKS

W. HEFFER & SONS, LTD, CAMBRIDGE

Licensed Valuers for Probate

Telephone: 862 Telegrams and Cables: "Heffer Cambridge"



Supersensitive Photo-Cells

Having recently been favoured with the exclusive representation in British Territories of Messrs The G.-M. LABORATORIES INC., Belmont Avenue, Chicago, U.S.A., we are now, more than ever, in a position to offer you advantageously and promptly your requirements on light-sensitive devices.

The G.-M. Company are the absolute pioneers in the manufacture of P.E.-Cells. Types are available for every purpose for which such Cells are employed, each being the best procurable. Special features include:

GREAT SENSITIVITY · QUIET OPERATION · EXCEPTIONALLY LONG LIFE · SMALL SIZE · ENGLISH OR AMERICAN BASES · NO LAG · NO "SCATTERING" · STABILITY · LOW PRICES

REQUEST TECHNICAL BULLETIN
G.M.-31, PLEASE

CLAUDE LYONS, LTD.
40 Buckingham Gate, London, S.W.1

4 POINTS
ABOUT VITREOSIL

1. Its expansion is very low, very regular, and there is no thermal or mechanical hysteresis.
2. It is an excellent electrical insulator, especially at high temperatures.
3. It is chemically inert to acids, hot, cold, weak, strong or mixed, except phosphoric and fluoric.
4. It is extremely transparent right into the short ultra-violet portion of the spectrum.

Will any of these properties assist you in your work?

The Thermal Syndicate Ltd.
VITREOSIL WORKS, WALLSEND-ON-TYNE
(Est. over quarter of a century)
London Depot: THERMAL HOUSE, OLD PYE STREET, S.W.1

PROCEEDINGS OF THE PHYSICAL SOCIETY

Advertisement Rates

The charges per insertion for advertisements in the *Proceedings* are as follow:

Whole page	£5. 0*s*. 0*d*.
Half page	£3. 0*s*. 0*d*.
Quarter page	£1. 15*s*. 0*d*.
Eighth page	£1. 0*s*. 0*d*.

A reduction of 20 % in these charges is allowed for five consecutive similar insertions. Rates for special positions will be quoted on application.

¶ *All communications respecting advertisements should be sent to the* ASSISTANT SECRETARY, THE PHYSICAL SOCIETY, 1 LOWTHER GARDENS, EXHIBITION ROAD, LONDON, S.W. 7.

Apparatus of various kinds for the scientific worker in PHOTOGRAPHY

The cheap and ever popular
IMPROVED
S.S. DENSITY METER
(VISUAL OPAL CONTACT)

Latest model with focussing eyepiece will give accuracy of reading to within ±0·025

PRICE COMPLETE 55/-
(*BOOKLET FREE*)

Experimental light filters carefully made to specified absorption and transmission

THE
E.S.S. COLOUR FILTER Co.
1 Montague Street, W.C. 1

H. K. LEWIS & CO. LTD. PUBLISHERS & BOOKSELLERS

BOOKSELLING DEPARTMENT—A thoroughly up-to-date and representative stock of Scientific and Technical Works always on hand. Catalogues on application.

FOREIGN DEPARTMENT—Prompt attention to orders and enquiries.

STATIONERY DEPARTMENT—Scientific and General: Loose-leaf Note Books, Record Cards, Filing Cabinets, etc.

SECOND-HAND DEPARTMENT—140 Gower Street: Telephone: Museum 4031. Large and varied stock of books on Science generally. Catalogues post free on request.

The New Premises
Corner of Gower St and Gower Place.

SCIENTIFIC & TECHNICAL CIRCULATING LIBRARY

Annual Subscription: Town or Country
from One Guinea

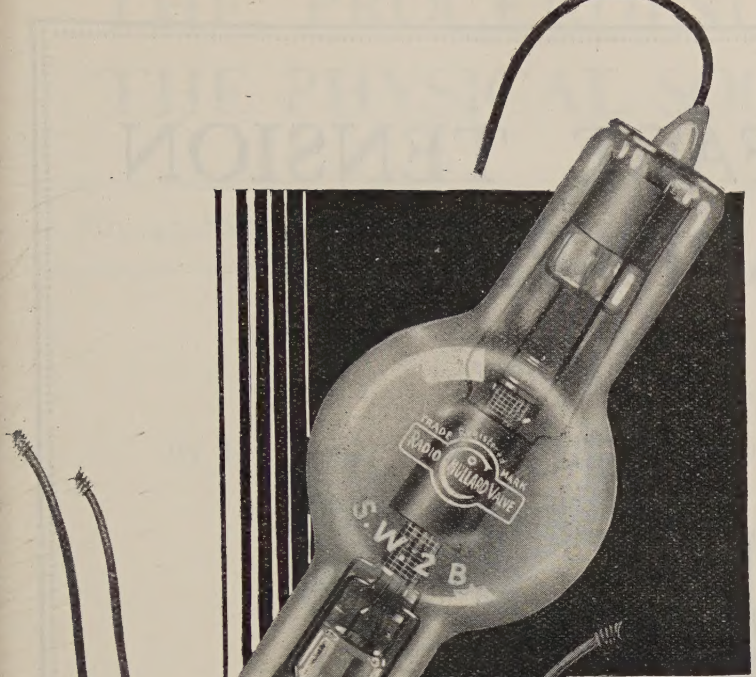
The Library is particularly useful to SOCIETIES and INSTITUTIONS, and to those engaged on special Research Work.

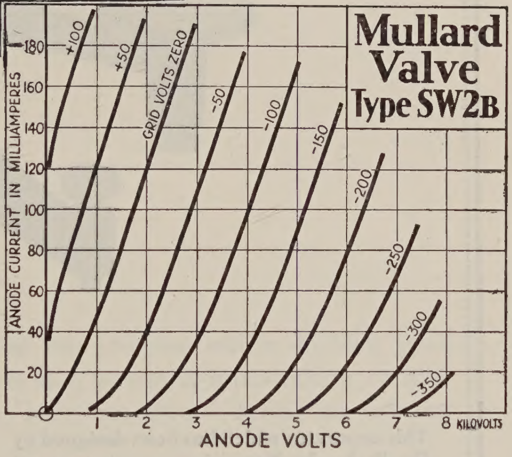
Full Prospectus on Application

Reading Room (first floor) open daily to Subscribers.

Bi-monthly list of additions to the Library Post Free on Application.

H. K. LEWIS & Co. Ltd., 136 Gower Street, London, W.C. 1
Telegrams: 'PUBLICAVIT, EUSROAD, LONDON' *Telephone*: MUSEUM 7756 (3 lines)





MULLARD SHORT WAVE TRANSMITTING VALVE

TYPE S.W.2B.

Type S.W.2B. is a medium power transmitting valve designed for operation on wavelengths down to 15 metres at a maximum continuous anode dissipation of 200 watts. When working at 15 metres the input power should not exceed 240 watts at 2,000 volts.

OPERATING DATA & CHARACTERISTICS.

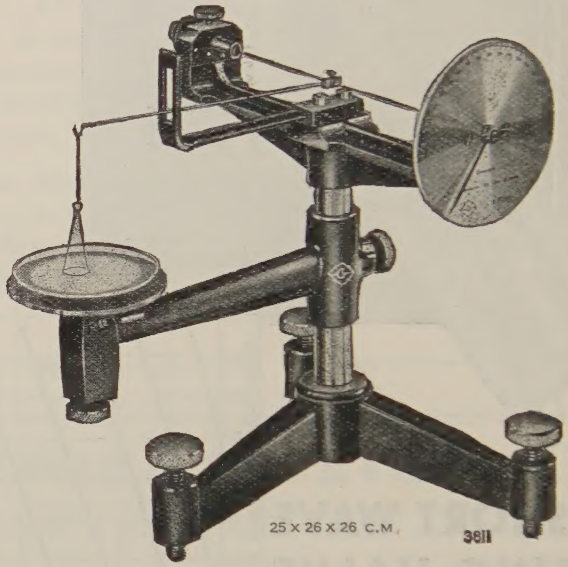
Filament Voltage	12.0 volts.
Filament Current	5.5 amps.
Max. Anode Voltage	3,000 volts.
Max. Anode Dissipation ... (Continuous operation)	200 watts.
Total Emission	450 mA.
Amplification Factor	20
Impedance	12,500 ohms.
PRICE	**£11 : 10 : 0**

Mullard

THE · MASTER · VALVE

Advt. The Mullard Wireless Service Co. Ltd., Mullard House, Charing Cross Road, London, W.C. 2. *Arks*

SURFACE TENSION APPARATUS



This apparatus which has been designed by Dr P. L. du Nouy, incorporates recent improvements. It is used for rapidly and accurately determining the surface tension of liquids. The method is simple, requires only a small quantity (about 1 c.c.) of the substance being tested, and is applicable to practically all kinds of liquids. The instrument is calibrated to read directly in dynes per cm.

A modified instrument is also available for determining the interfacial tension between two liquids.

Further details are given in our
LIST No. V–100
which will be sent on request.

CAMBRIDGE
INSTRUMENT CO. LTD.
WORKS:- LONDON & CAMBRIDGE
Head Office & Showrooms
45 GROSVENOR PLACE
LONDON, S.W.1

32

ERRATUM

Page 444, *for* "Makin" *read* "Mather."

THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 43, PART 5 *September* 1, 1931 NO. 240

COHESION

BY J. E. LENNARD-JONES, The University, Bristol

A Lecture delivered before the Society on May 1, 1931.

§ 1. INTRODUCTION: NEW IDEAS IN PHYSICS

THERE are in nature, as in politics, two opposing forces. One of these aims at a peaceful consolidation and the other at a more active and probably more spectacular disruptive process. In nature it is cohesion between atoms which tends to produce condensation and solidification, and temperature which tends to produce dissociation, first of solids into liquids and then into isolated molecules, then of molecules into atoms and finally into electrons and protons (as in the hotter stars).

Temperature is a manifestation of kinetic energy and cohesion of potential energy, and the interplay of these two forms of energy is responsible for many of the observed physical properties of matter. A knowledge of the nature of cohesion is thus a necessary step towards an understanding of these physical properties. In this lecture I propose to review some of the progress which the new wave mechanics has made possible in this direction and, by way of introduction, to refer to some of the new conceptions which have been introduced during the last few years.

First, there is the main idea of wave mechanics that it is impossible to follow the electron in all its ways. Instead of supposing that the electron of an hydrogen atom steadily pursues for all time a definite track or orbit, we are now content to know the probability that it will do this or do that. We represent the electron by continuous distributions—probability patterns. To each such pattern there corresponds a definite average energy and normally the electron stays in the pattern of lowest energy. The density of the pattern at any point of space is a measure of the probability that the electron shall be found there. The probabilities become infinitesimally small outside regions measuring one hundred-millionth of a centimetre, so that the electrons of an atom may be regarded as almost always within this small region. This is the interpretation to be given to the "size" of an atom from the new point of view*.

The mathematical theory does not give these density patterns directly. The wave equation gives the possible energy levels and certain mathematical functions, ψ usually called wave functions and denoted by ψ, associated with them. The quantity here denoted by ψ is a function of the three coordinates used to specify the position of the electron in space. When ψ is a real quantity, its square is interpreted as a measure of the density of the probability pattern, just as the square of the amplitude (and not the amplitude itself) is a measure of the intensity of a sound or light wave. When ψ contains the square root of -1, the square of the amplitude of ψ, viz. $\bar{\psi}$ $|\psi|^2$, or the product of ψ with its conjugate complex function, viz. $\psi\bar{\psi}$, is taken to be the appropriate measure of the probability of a given configuration.

§ 2. PAULI EXCLUSION PRINCIPLE

The hydrogen is particularly simple to work out because there is only one electron. It is equally easy to work out the patterns for one electron alone in the presence of a nucleus of charge Ze. The patterns are similar to those of hydrogen, but are contracted in the ratio 1 to Z everywhere.

If electrons are added one at a time to a nucleus of charge Ze until the whole structure is neutral and thus complete, we must inquire what happens to the electrons after the first. There is nothing in the wave mechanics, as formulated at present, to prevent all the electrons taking up the same pattern. The density of the electrons might be regarded as identical and superimposed, except for the electrostatic repulsion between them which would tend to swell out the pattern again.

We know from experience, however, that all the electrons of an atom do not assume the same pattern, and we have had to invoke an entirely new principle, first enunciated by Pauli, and now generally referred to as the *exclusion principle*. This principle asserts that there are never more than two electrons in the same pattern; it goes further by asserting that it is not sufficient to describe patterns in terms of the three spatial coordinates of an electron, but that a fourth coordinate must be introduced. This fourth coordinate can take only two discrete values, so that the patterns we have described up to now are to have a further property added to them which will double their number. It is as though the patterns had colour as well as shape. Actually it is usual to attribute a spin to the electron, and to suppose that the axis of the spin can take up either of two quantized directions. The exclusion principle then asserts that there is only one electron, described by its four coordinates, in every pattern. In building up atoms by the addition of one electron at a time, the electrons arrange themselves in those patterns which respect the exclusion principle, and at the same time take up the configuration of least energy. The application of this principle accounts in a very beautiful way for the main features of atoms and molecules.

---

* At this stage of the lecture, a number of diagrams of patterns of the excited states of the hydrogen atom were shown. It was intended to reproduce these, but since the lecture, a number of similar pictures have been published by H. E. White, *Phys. Rev.* 37, 1416 (1931), to which reference may be made.

§ 3. PRINCIPLE OF IDENTITY OF ELECTRONS

In this addition of electrons to an atom, we have tacitly assumed that each electron persists in one pattern. But so far as is known, electrons are identical, and a system in which two electrons are interchanged is indistinguishable from its original state. This principle of the *identity of electrons* has proved to be of great importance. A method must be found of introducing this fact into the mathematics, and this was first done about the same time by Dirac and Heisenberg.

If we suppose that there are N electrons in an atom and that the wave functions associated with the patterns which they occupy are $u_1, u_2, \ldots u_N$, these functions including spin as well as space coordinates, then the wave function of the whole system must be taken to be*

N

u_N

$$\Psi = \begin{vmatrix} u_1(1), & u_2(1), & \ldots & u_N(1) \\ u_1(2), & u_2(2), & \ldots & u_N(2) \\ \vdots & \vdots & \ldots & \vdots \\ u_1(N), & u_2(N), & \ldots & u_N(N) \end{vmatrix}$$

Ψ

In this determinant $u_N(1)$ indicates that the four coordinates of electron 1 are to be introduced into the Nth function, and so on. Now if two electrons 1 and 2 are interchanged, the effect on the determinant is to interchange rows 1 and 2, and this has the effect of changing only the sign of Ψ. Furthermore, if we suppose two wave functions u_1 and u_2 to be the same, two columns of the determinant become identical and the determinant vanishes. The mathematical expression of the Pauli exclusion principle is thus that no two of the wave functions $u_1, \ldots u_N$ may be the same. The determinantal form of Ψ thus takes into account the identity of the electrons and the exclusion principle at the same time.

$u_N(1)$

Actually when the electrostatic repulsions between electrons in an atom are taken into account, we cannot regard the wave function as made up of N different functions $u_1 \ldots u_N$, each containing only the coordinates of one electron. All that we can be certain of is that the complete wave function, when found, must have the same properties as the determinant as regards the interchange of electrons and the exclusion principle. It has not been possible, however, as yet to deal mathematically with functions more complicated than the determinant.

The probability distribution of the N electrons is now given by $\Psi\overline{\Psi}$, which is a generalization of the probability distribution for one electron. When the two determinants Ψ and $\overline{\Psi}$ are multiplied together, we find

---

* This is subject to the condition that there be not several functions of this type with the same energy. It is possible to write the wave function in the form given above for most atoms in their state of lowest energy.

$$\Psi\overline{\Psi} = \begin{vmatrix} \rho(1, 1), & \rho(1, 2), & \ldots & \rho(1, N) \\ \rho(2, 1), & \rho(2, 2), & \ldots & \rho(2, N) \\ \vdots & \vdots & \ldots & \vdots \\ \rho(N, 1), & \rho(N, 2), & \ldots & \rho(N, N) \end{vmatrix}$$

$\rho(1, 2)$ where*

$$\rho(1, 2) = \sum_j \bar{u}_j(1)\, u_j(2).$$

We note that $\rho(1, 1)$ is the sum of terms like $\bar{u}_j(1)\, u_j(1)$ which are density functions of electron 1 in the different patterns; in fact, we have

$$\rho(1, 1) = \sum_j \rho_j(1, 1),$$

and we should be justified in superimposing the density patterns if it were not for the terms like $\rho(1, 2)$. These indicate to us that we must no longer expect to express the charge density in three dimensions (or four, including spin), but we must use a six-dimensional function (or an eight-dimensional one if we include spin). This is not surprising. In the older theories, when electrons were assumed to be pursuing orbits, we needed a knowledge not only of space coordinates but also of the components of velocity of the electrons to specify their configuration completely. Now that we have given up the idea of attributing definite velocities and space coordinates to electrons simultaneously, we must not be surprised to find the six-dimensional character of the probability configuration appearing in another form.

§ 4. ELECTRON-DISTRIBUTIONS IN ATOMS

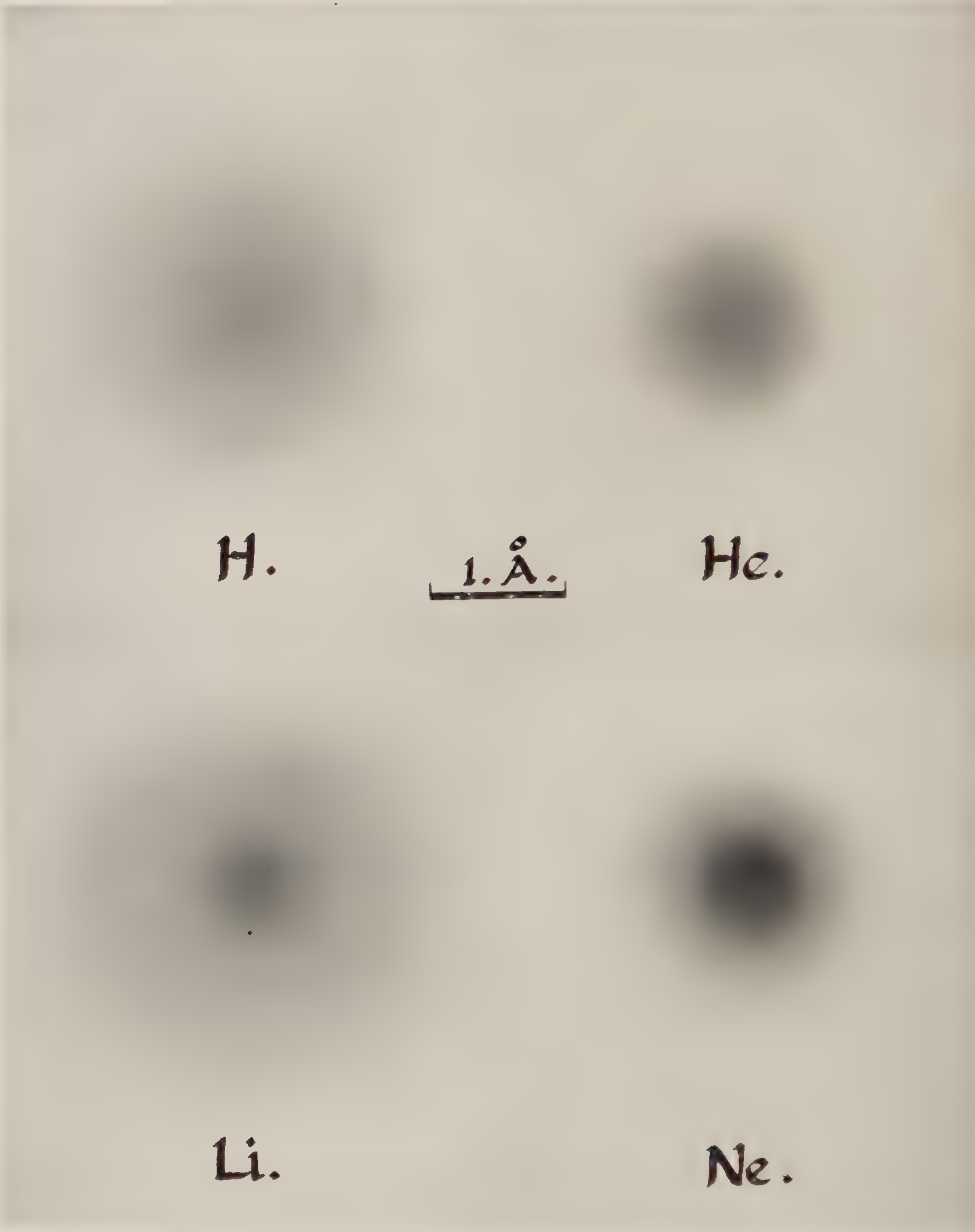
The expression given above for $\Psi\overline{\Psi}$, multiplied by elements of volume $d\tau$ $d\tau_1, d\tau_2, \ldots d\tau_N$, in the configuration space of each electron, may be interpreted as the probability that an electron (we do not specify which one) shall be found in $d\tau_1$, another in $d\tau_2$, and so on simultaneously†. The probability that an electron shall be found in $d\tau_1$, irrespective of the position of the other electrons, is obtained by integrating $\Psi\overline{\Psi}$ over the configuration space of electrons 2 to N. In the integration each electron configuration is to be counted only once, so that if $d\tau'$ indicates one specified element of volume and $d\tau''$ another, $d\tau_1'\, d\tau_2''$ is to be taken to be the same as $d\tau_1''\, d\tau_2'$. The result of the integration is $\rho(1, 1)\, d\tau_1$ or $\sum_j \rho_j(1, 1)\, d\tau_1$, and is thus the same as the superposition of the separate patterns ρ_1 to ρ_N‡. In this

---

* This form of the function $\Psi\overline{\Psi}$ has been given recently by Dirac, *Proc. Camb. Phil. Soc.* **27**, 240 (1931); cf. also Lennard-Jones, *Proc. Camb. Phil. Soc.* **27**, 469 (1931).

† P. A. M. Dirac, *loc. cit.*

‡ This result holds when the functions u_1 to u_N are normalized and orthogonal, that is, $\int \bar{u}_k u_l\, d\tau = \delta_{kl}$. For most atoms in their normal state, the wave functions can be adjusted to satisfy this condition.


H.
1. Å.
He.
Li.
Ne.

sense we may construct pictures of many-electron atoms, and these pictures represent the probability of finding *an* electron in any element of volume in ordinary space.

When the process is carried out, it appears that many atoms—more than were previously suspected—may be considered to be spherically symmetrical. Of the first ten atoms of the periodic table, six may be so regarded. They are hydrogen, helium, lithium, beryllium, nitrogen* and neon. Diagrammatic pictures of some of these atoms are given on the accompanying plate†. They have been calculated from some approximate wave functions given by Slater‡. The pictures cannot be regarded as accurate but they give a fair idea of the relative "spread" of the various atoms. The inert gas atoms, occurring at the end of a group of the periodic table, are usually the most compact atoms of that group.

The spread of these atoms may be gauged also from figure 1. The contours give the probability of finding an electron *outside* the contour. The first is 0·2—that is, the probability of finding an electron outside it is 1 in 5. The second, third... are 0·4, 0·6.... Outside the contour 1·0, there is a *certainty* of finding one electron; outside the contour 1·2 there is a probability of finding two electrons simultaneously. The spread of lithium, which combines with others in the solid state to form a metal, is in striking contrast to that of neon, although the latter contains many more electrons. Boron in its normal state has one electron in a $2p$-state, or one with quantum numbers $n = 2$, $l = 1$, $m = 1$, 0 or -1. The corresponding probability patterns are asymmetrical. The one with quantum numbers 2, 1, 0 consists of two blobs of electron charge situated symmetrically with respect to the nucleus. The plane of symmetry contains no charge, while a line through the nucleus perpendicular to this plane of symmetry passes through the centres of the blobs. Along this line the electron charge increases from zero to a maximum and then falls away to zero§. This line may be referred to as the axis of the pattern. Those with quantum numbers (2, 1, 1) and (2, 1, − 1) are like anchor rings. The concentration of charge in each is zero along the axis, and has a maximum along the core, from which it decreases to zero in each direction. The axis of the ring coincides with the axis of the (2, 1, 0) pattern so that the maximum concentration of the (2, 1, 1) pattern lies in the plane of zero concentration of the (2, 1, 0) pattern.

Carbon in its normal state may be regarded as having one of its two outer electrons in the (2, 1, 0) pattern and the other in either the (2, 1, 1) or the (2, 1, − 1) pattern, while the two electron spins are the same‖. The electron distribution thus consists of an anchor ring and two "balls" of charge on its axis above and below the nucleus, all of which is superimposed on a background due to the inner electrons, which is spherically symmetrical.

---

* In its normal state, that is, in the ^4S state.

† I am greatly indebted to Mr H. H. M. Pike of the H. H. Wills Physical Laboratory, Bristol, for these pictures, as also for those in figure 1, and for the calculations involved in making them.

‡ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

§ Cf. H. E. White, *loc. cit.*

‖ The normal state of the carbon atom is a ^3P state.

Nitrogen has one outer electron in a (2, 1, 0) pattern, another in a (2, 1, 1) pattern and a third in a (2, 1, - 1) pattern. These three patterns when superimposed give a distribution which is spherically symmetrical. The spins of these three outer electrons in the normal state of the nitrogen atom are the same, for this configuration gives the lowest energy (the ^4S state).

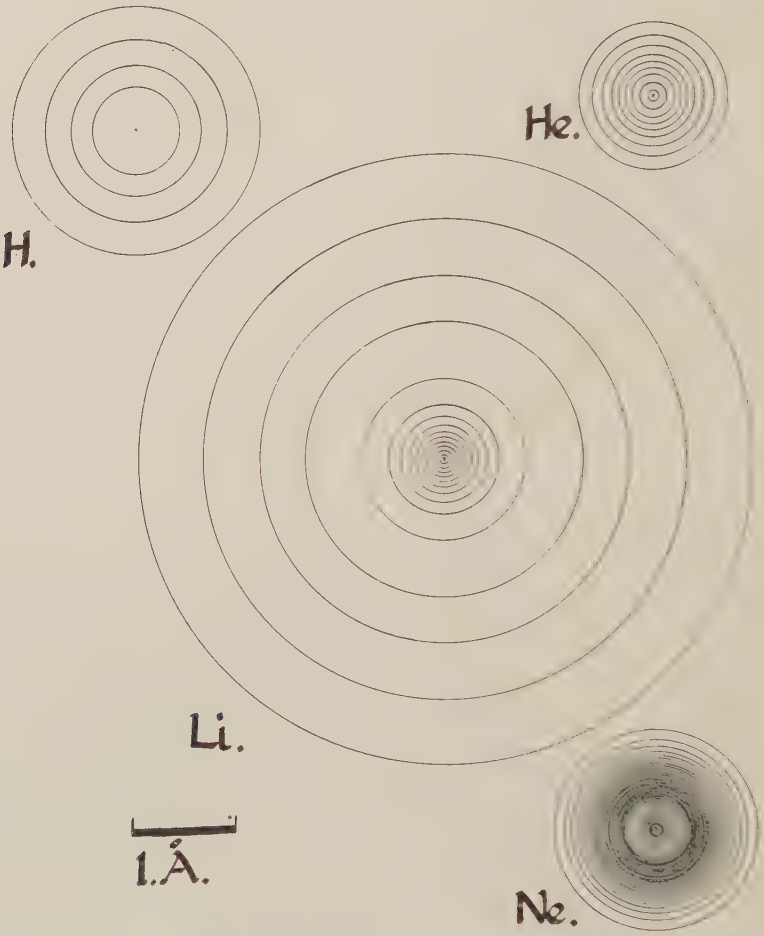


Fig. 1. The "spread" of the atoms hydrogen, helium, lithium and neon.

Neon, which has six electrons in the $2p$-state, has two electrons, one of each spin, in each of the patterns (2, 1, 1), (2, 1, 0) and (2, 1, − 1). It also is spherically symmetrical. Flourine has one less electron than neon, and so we may regard it as an atom which requires one electron to complete its spherical symmetry*. It is an atom with a "hole" in it, and the "hole" is probably a (2, 1, 0) pattern†.

---

* This property is connected with the affinity which fluorine has for an electron.

† Cf. J. E. Lennard-Jones, *Trans. Faraday Soc.* **25**, 668 (1929).

Oxygen has two "holes," one of which is probably a (2, 1, 0) and the other a (2, 11), or a (2, 1, − 1) pattern. Like divalent carbon, its normal state is a ^3P state, though now this state may be attributed to two *holes*, whereas in carbon it is due to the two *electrons*. In this sense oxygen may be regarded as the counterpart of divalent carbon.

These pictures of atoms throw considerable light on their chemical properties and elucidate the problem of molecular structure, to which we shall refer below.

§ 5. PRINCIPLE OF MINIMUM ENERGY

To the new principles already discussed, we must add an old one, viz., the principle of minimum energy; an atomic or molecular system tends to take up the state of lowest energy. This is of fundamental importance in the subject of cohesion.

§ 6. TYPES OF COHESIVE FORCES

The physical and chemical properties of matter show that cohesive forces fall into certain definite categories. Helium must be cooled down to − 269° C. before it begins to aggregate, whereas hydrogen exists in the diatomic form at ordinary temperatures. All the rare gases are similar to helium in exhibiting this weak cohesion. Neon liquifies at about − 240° C. and argon at − 186° C. The weak attractive fields of these gases is responsible for their small departure from the ideal gas laws, and as they were first investigated by van der Waals, they may conveniently and fittingly be referred to as *van der Waals attractive fields*. This type of attraction probably exists between all atoms and molecules, as will appear in the next paragraph, but it is usually masked by other large attractive fields of a different type.

The cohesive forces which hold together the atoms of a hydrogen or a nitrogen molecule are about a thousand times as great as those which two helium atoms exert on each other, even when they are neighbours in the solid form. These forces are the familiar *homopolar attractive fields* of the chemist. At the same time it should be pointed out that the *molecules* of hydrogen and nitrogen behave like the inert gases as regards liquefaction and solidification and it is almost certain that such molecules are held together in the condensed form by van der Waals forces. It requires only about 500 calories to evaporate one gram molecule of solid hydrogen, whereas 100,000 calories per gram molecule are required to dissociate 1 gram molecule of molecular hydrogen.

There is distinct evidence that in some solids, such as NaCl, there is a migration of an electron from one atom (such as an alkali) to another atom (such as a halogen). The atom which loses an electron becomes positively charged and the other negatively charged. There is thus a net electrostatic attraction between neighbouring atoms and this produces a very firm structure, which is difficult to disrupt. When such solids are vaporized (usually at high temperatures) the vapour is diatomic. Such molecules may be said to be held by *ionic attractive fields.*

There are other solids which are also difficult to melt and to vaporize, but which stand in a different class from the ionic solids or salts. They have other properties not possessed by the salts in that they are good conductors of heat and electricity and, so far as is known, are monatomic in the vapour state. These solids, the metals, stand in a class by themselves and the forces holding them together may be called *metallic attractive fields.*

Intimately connected with the subject of cohesion is the question why atoms ever repel each other. The very existence of matter leads us to postulate that when atoms approach very near to one another they begin to repel. The resistance which solids offer to compression is evidence and indeed a measure of the repulsive forces between atoms. A theory which explains cohesion may be expected also to explain *intrinsic repulsive fields* and this proves to be the case.

§ 7. THE NATURE OF VAN DER WAALS FIELDS

Although it is sufficient for many purposes to represent electrons in atoms as continuous distributions, such representations are not, of course, accurate. It is only the average which is continuous, and there must be rapid fluctuations about this average, corresponding to the motion in a classical sense of the electrons within the atom. Without it, van der Waals fields, as we know them, would not exist. Two hydrogen atoms in their normal state, for example, are each represented by a spherically symmetrical distribution, and as each is neutral, the electrostatic potential of the one distribution on the other at a large distance apart is vanishingly small. Nor can van der Waals fields be interpreted in terms of a static disturbance of the continuous distribution. These fields have often been attributed vaguely to polarization. But this polarization cannot be a static one, for if it were, each atom so polarized could be represented by a small permanent dipole at its centre. As the interaction in the case of equal atoms is symmetrical, the dipoles produced must be symmetrical about a plane midway between them. They must therefore point either towards or away from each other. In either case they cause repulsion. Van der Waals fields, as we shall show, are due to a *dynamic* polarization. The motion of the electrons in one atom modifies that of the electrons in the other in such a way that *they tend on the average to move in phase.* An important consequence is that van der Waals fields to a close approximation are additive, even when one is surrounded symmetrically by several others. Although there was evidence from many sources that these fields were additive, this property could not be deduced from a theory of static polarization.

The nature of van der Waals fields may probably be brought out most clearly by means of a simple molecular model. Suppose that an atom is represented by a linear oscillator, that is, by an electron vibrating linearly about the nucleus. Such a system requires only one coordinate z to specify it. The appropriate Schrödinger equation is then

z

$$\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-\tfrac{1}{2}kz^2)\psi=0,$$

E

where m is the mass of the electron, and $\frac{1}{2}kz^2$ is the potential energy of the electron. On the classical theory, an oscillator of this type, subject as it is to a restoring force of kz, would have a frequency given by

m, k

$$2\pi\nu_0=\sqrt{k/m}.$$

ν_0

The solution of the wave equation is well known. It consists of a set of discrete values for E, viz., $E=(n+\frac{1}{2})h\nu_0$, where n is any integer. In the state of lowest energy, the appropriate value of ψ is given by

n

$$\psi=(2\kappa\,\nu_0/\pi)^{\frac{1}{4}}\,e^{-\kappa\nu_0 z^2}$$

where $$\kappa^2=2\pi\,m/h.$$

κ

The equation is written in such a form as to bring out the dependence of ψ on the frequency ν_0 for a purpose which will be seen later.

The "smeared-out" pattern for the electron in this case is thus a Gaussian error curve, symmetrical about the origin.

We suppose now the oscillator to be subject to a uniform electric field F, so that the potential energy becomes $\frac{1}{2}kz^2-eFz$ or $\frac{1}{2}k(z-eF/k)^2-e^2F^2/2k$. The appropriate wave equation can be written

F

$$\frac{\partial^2\psi}{\partial\xi^2}+\frac{8\pi^2m}{h^2}\left(E+\frac{e^2F^2}{2k}-\tfrac{1}{2}k\xi^2\right)\psi=0,$$

which has the same form as the original equation, except that ξ, which $=z-eF/k$, now takes the place of z.

ξ

The energy values are $E=(n+\frac{1}{2})h\nu_0-e^2F^2/2k$. The last term gives the change of energy due to the field—the so-called polarization energy.

$$\textit{Polarization energy}=-e^2F^2/2k.$$

In terms of the coefficient of polarizability α, the polarization energy is $-\frac{1}{2}\alpha F^2$ by definition, so that $\alpha=e^2/k$.

α

The corresponding density pattern is proportional to $e^{-2\kappa\nu_0(z-eF/k)^2}$, which is the same as the original one, except for a displacement of the maximum through an amount eF/k in the direction of the field. This represents a static polarization.

We next suppose the oscillator to be subject to the field of a distant parallel rigid dipole of strength μ at a distance R. The potential of the electron is then $-2\mu ez/R^3$ and is like a parallel field except that the constant of proportionality depends on R. The theory of the preceding paragraph applies if F is replaced by $2\mu/R^3$, and so the energy of the oscillator, being proportional to the square of F, is now proportional to μ^2R^{-6}.

μ, R

$$\textit{Polarization energy}=-2e^2\mu^2/kR^6.$$

Moreover, the energy being negative indicates attraction. The polarization of the oscillator is again a static one.

If now we suppose the dipole μ to fluctuate in value and to change in sign independently of the original oscillator (though this is an artificial assumption), the polarization of the oscillator is always such as to give an attraction proportional to R^{-6}; in fact, we have

$$\textit{Average polarization energy} = -\,2e^2\overline{\mu^2}/kR^6.$$

The polarization is now a fluctuating one and may be described as a *dynamic* one.

Actually the second dipole cannot be regarded as fluctuating independently of the first. It also will be subject to a dynamic polarization, and the two systems must be regarded as one complete coupled system. The method, however, prepares the way for a more accurate treatment* and suggests that two such oscillators will tend to move in phase.

The complete wave equation for two equal oscillators, each vibrating along the axis of z under each other's influence, is

$$\frac{\partial^2\psi}{\partial z_1^2} + \frac{\partial^2\psi}{\partial z_2^2} + \frac{8\pi^2 m}{h^2}\left(E - \tfrac{1}{2}kz_1^2 - \tfrac{1}{2}kz_2^2 + \frac{2e^2 z_1 z_2}{R^3}\right)\psi = 0,$$

and this can easily be transformed to new variables

ξ_1, ξ_2

$$\xi_1 = (z_1 + z_2)/\sqrt{2}, \quad \xi_2 = (z_1 - z_2)/\sqrt{2},$$

$$\frac{\partial^2\psi}{\partial \xi_1^2} + \frac{\partial^2\psi}{\partial \xi_2^2} + \frac{8\pi^2 m}{h^2}\left(E - \tfrac{1}{2}k_1\xi_1^2 - \tfrac{1}{2}k_2\xi_2^2\right)\psi = 0,$$

k_1, k_2 where

$$k_1 = k - 2e^2/R^3, \quad k_2 = k + 2e^2/R^3.$$

The possible energy values of the equation are

n_1, n_2

$$E = (n_1 + \tfrac{1}{2})\,h\nu_1 + (n_2 + \tfrac{1}{2})\,h\nu_2,$$

where

ν_0, ν_1, ν_2

$$\nu_1 = \frac{1}{2\pi}\sqrt{(k_1/m)} = \nu_0\sqrt{(1 - 2e^2/kR^3)}, \quad \nu_2 = \nu_0\sqrt{(1 + 2e^2/kR^3)}.$$

This transformation is accurate and valid as long as ν_1 is real, that is as long as $2e^2/kR^3 < 1$. This implies that R must be greater than $(2\alpha)^{\frac{1}{3}}$. For the state of lowest energy, we thus get

$$\begin{aligned} E &= \tfrac{1}{2}h\,(\nu_1 + \nu_2) \\ &= h\nu_0\,(1 - e^4/2k^2R^6), \end{aligned}$$

if the square roots be expanded, as they can for large R. This indicates that the energy of interaction of the dipoles, or the

$$\textit{van der Waals polarization energy} = -\,h\nu_0 e^4/2k^2R^6,$$

and that there is an attractive *force* proportional to the inverse seventh power of the distance.

---

* Cf. F. London, *Zeit. f. phys. Chem.* **11**, 222 (1930).

The wave function for the whole system for this lowest state is equal to the product of the appropriate functions in ξ_1 and ξ_2, viz.,

$$\begin{aligned} \psi &= (4\kappa^2\, \nu_1 \nu_2/\pi^2)^{\frac{1}{4}}\, e^{-\kappa(\nu_1\xi_1^2+\nu_2\xi_2^2)} \\ &= (2\kappa/\pi)^{\frac{1}{2}}\, (\nu_1\nu_2)^{\frac{1}{4}}\, e^{-\kappa\nu_0(z_1^2+z_2^2)}\, e^{(\kappa\nu_0 e^2/k)(2z_1z_2/R^3)} \\ &= (\nu_1\nu_2/\nu_0^2)^{\frac{1}{4}}\, \psi_0\, e^{-(\kappa\nu_0/k)v}, \end{aligned}$$

where ψ_0 is the corresponding wave function before interaction, and v is the potential ψ_0, v of interaction $(-\,2e^2\, z_1 z_2/R^3)$.

The probability of a specified configuration, that is, a specified z_1 and a specified z_2, is given by the square of ψ, and is thus proportional to $\psi_0^2\, e^{-\beta v}$. When v is negative (indicating attraction between the dipoles), the probability is greater than ψ_0^2 and when v is positive (indicating repulsion between the dipoles), the probability is less than ψ_0^2.

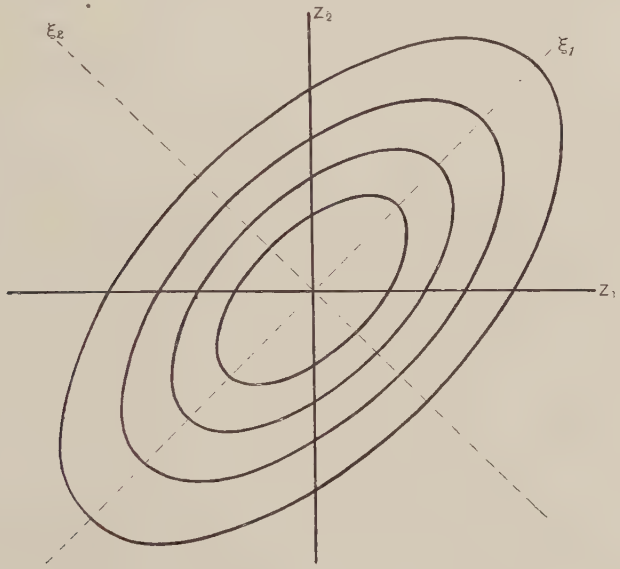


Fig. 2. The probability function for two interacting linear oscillators.

This result can be represented diagrammatically in a two-dimensional space, as shown in figure 2. The distribution function, being proportional to $e^{-2\kappa(\nu_1\xi_1^2+\nu_2\xi_2^2)}$, is like a ridge with its maximum at the origin, and with elliptical contours. The major axes of the ellipses are $\xi_2 = 0$ or $z_1 = +\,z_2$, and the minor axes $z_1 = -\,z_2$. The corresponding distribution without interaction is a round-topped mountain with circular contours. The probability of finding z_1 and z_2 with the same sign has increased, while that of finding them with the opposite sign has decreased. In other words, the interacting dipoles tend on the average to move in phase.

A similar treatment can be given for two three-dimensional oscillators*. Let the line joining the centres of the oscillators be in each case the axis of z as before,

---

* F. London, *loc. cit.*

x, y and let any convenient parallel sets of axes x and y be chosen in planes perpendicular to this axis through the respective centres. The mutual potential energy of the oscillators is then

$$V = e^2 (x_1 x_2 + y_1 y_2 - 2z_1 z_2)/R^3.$$

The probability-distribution function can now be represented only in six-dimensional space. It appears that z_1 and z_2 tend to have the same sign (as before), while x_1 tends to be opposite to x_2, and y_1 opposite to y_2. These are just the configurations for which the oscillators attract. Hence we may say that two systems tend to interact in such a way that the attraction is a maximum. It is in the generalized sense that we use the expression "tend to move in phase," for actually in this example the x's and y's tend to be out of phase in the usual sense.

These simple examples, which can be worked out accurately, serve to bring out the essential nature of van der Waals fields, and we may presume that in other more complicated cases, where the mathematics is more difficult to interpret, the attraction is due to a *sympathetic* movement of the electric charge.

The mathematical calculations for actual atoms are not easy. Wang* was the first to attempt the calculation of the van der Waals fields of two hydrogen atoms. He showed that the asymptotic form of the interaction of two hydrogen atoms was like that of two dipoles, and used this additional potential as a perturbation of the wave equation of two normal atoms. He thus showed that the attractive force between them at large distances varied inversely as the seventh power of the distance. The numerical value has not, however, been confirmed by later investigations. Recently Eisenschitz and London† have given a method of calculating fields of this type for any atoms, which is based on the second approximation of the usual perturbation theory. (The first approximation of this theory vanishes at large interatomic distances). The wave function of the system is expressed in terms of certain selected unperturbed wave functions of the two atoms. The method is rather unwieldy and the authors themselves expressed the hope that some simpler method would be found. The problem has also been considered by Lennard-Jones‡, Hassé§, and Slater and Kirkwood ‖. The first of these authors uses a modified form of the perturbation theory which considerably simplifies the calculation of the van der Waals fields of two hydrogen atoms, while the second two use specially adapted variation methods. In each case the *potential* of the attractive field is of the form $-\lambda R^{-6}$, and the values obtained for λ are as follows:

Eisenschitz and London ...	$6{\cdot}04 . 10^{-60}$
Lennard-Jones	$6{\cdot}04 . 10^{-60}$
Hassé	$6{\cdot}05 . 10^{-60}$
Slater and Kirkwood	$6{\cdot}05 . 10^{-60}$

These values of λ give the attraction in ergs when R is measured in centimetres.

---

* S. C. Wang, *Phys. Zeit.* **28**, 663 (1927).

† R. Eisenschitz and F. London, *Zeit. f. Phys.* **60**, 491 (1930).

‡ J. E. Lennard-Jones, *Proc. R.S.* A, **129**, 598 (1930).

§ H. R. Hassé, *Proc. Camb. Phil. Soc.* **27**, 66 (1931).

‖ J. C. Slater and Kirkwood, *Phys. Rev.* **37**, 682 (1931).

The calculations for hydrogen atoms are valid, of course, only at large interatomic distances. At smaller distances the exchange phenomenon, referred to below, comes into prominence, and leads eventually to the formation of the diatomic molecule. The exchange forces, however, fall off very rapidly (as $e^{-\alpha r}/r$) and become small at distances at which the van der Waals fields are still important. It is unfortunate that in this case, where the theoretical calculations can be carried out with some accuracy, comparison with experiment is not possible.

An attempt has been made to extend the theory to more complicated atoms, but the main difficulty here is the lack of knowledge of the wave functions of these atoms. Even in the case of helium, the wave functions are only known approximately. London* has attempted to correlate the van der Waals fields of atoms with their coefficient of polarizability, but the correlation is only an approximate one, and only between certain rather wide limits can the magnitude of the fields be fixed by this method.

Hassé† has attempted the case of two helium atoms and has based his work on wave functions deduced by Hylleras‡ from a variation method. These wave functions are adjusted to make the energy of the helium electronic system a minimum and it does not follow that wave functions so deduced are valid over their whole range; in fact, it appears that they are probably fairly accurate near the nucleus (where the energy contributions are large) but less accurate in the outer parts of the atom. But it is just the outer parts of the atom which are most affected by outside fields, and so it is important that the wave function in those regions should be known accurately. Hassé finds that the Hylleras functions, which approximate best to the correct ionization potential of helium, do not give the best results for the polarization energy in a uniform electric field, which also is known experimentally. Similar calculations have been carried out for the van der Waals fields, but again there is a certain arbitrariness owing to the uncertainty of the Hylleras functions. The results obtained by Hassé are given below.

Slater and Kirkwood§ have given a further development of Hassé's method, also depending on the variation method. They work out the polarizability of helium and the van der Waals fields of two helium atoms by means of an approximate wave function, previously given by Slater‖. The results obtained so far for the attractive-force-constant of helium (λ in λR^{-7}) are as follows: λ

London	$7{\cdot}44 . 10^{-60}$¶
Hassé	$(7{\cdot}91–8{\cdot}21)\ 10^{-60}$
Slater and Kirkwood	$8{\cdot}94 . 10^{-60}$

Slater and Kirkwood give as well an expression for the field of two helium atoms at *close* distances. The potential curve obtained from their work is plotted in figure 3.

---

* F. London, *Zeit. f. phys. Chem.* **11**, 222 (1930).

† H. R. Hassé, *Proc. Camb. Phil. Soc.* **27**, 66 (1931).

‡ E. A. Hylleras, *Zeit. f. Phys.* **54**, 347 (1929).

§ J. C. Slater and Kirkwood, *Phys. Rev.* **37**, 682 (1931).

‖ J. C. Slater, *Phys. Rev.* **32**, 349 (1928).

¶ This figure is given as an upper limit, and is deduced from the formula given in the next paragraph, the observed value of the coefficient of polarizability being used.

Other inert gas atoms have been considered but the results can only be estimated roughly because the wave functions are not known sufficiently well. Both London and Slater-Kirkwood, unable to calculate the force-constants of these gases directly, attempt to correlate the force-constant with the coefficient of polarizability. Slater and Kirkwood give

$$\lambda = (\text{const.})\, N^{\frac{1}{2}} \alpha^{\frac{3}{2}},$$

while London gives

$$\lambda = (\text{const.})\, I \alpha^{2}.$$

λ, α
N
I

In each case λ is the constant of van der Waals field, and α is the coefficient of polarizability; in the first formula N is the number of electrons in the outer shell, and in the second I is the ionization potential. It is not known yet how far either formula is correct.

$\lambda_{(\text{rep.})}$, n

The attractive force constants of gases can also be determined from a study of the equation of state, as has been shown by the author[*]. A collected account of the methods used and the results obtained has already been published[†], but some new results, which have been worked out recently on the assumption of an attractive force of the type λR^{-7}, may appropriately be given here[‡]. The repulsive field, which comes into play at short distances, is represented by a force of the type $\lambda_{(\text{rep.})} R^{-n}$. Theoretical calculations of the type discussed in the next paragraph show that the repulsive field is more complicated than this and contains terms of the form e^{-aR}, but it falls off very rapidly with distance and can (in the case of helium at any rate) be represented, over the range which is most effective in atomic collisions, by a term of the type $\lambda_{(\text{rep.})} R^{-n}$.

$\lambda_{(\text{att.})}$

The equation of state alone does not determine the value of the index n in this repulsive field uniquely, but, for a given n, it determines the value of the constant $\lambda_{(\text{rep.})}$, and the attractive constant $\lambda_{(\text{att.})}$. Other methods have to be employed to single out the right value of n from the array of possible ones thus determined. The crystal spacing of the solidified gas or its heat of sublimation may be used for this purpose. In the accompanying table the results are given for $n = 10$, 11 and 13. The experimental material from which these results are derived is cited elsewhere[§], and later experimental results of Nijhoff[‖], and of Gibby, Tanner and Masson[¶] have been used as well. In table 1 are given calculated values of the closest distance of approach which these gases would have at absolute zero, if they set in the form of face-centred cubes. This is the form which would be expected theoretically for a force of the type $\lambda_{\text{rep.}} R^{-n} - \lambda_{\text{att.}} R^{-7}$,

---

[*] J. E. Lennard-Jones, *Proc. R.S.* A, **106**, 463 (1924), **107**, 157 (1925), **109**, 481 (1925), **112**, 214 (1926); J. E. Lennard-Jones and W. R. Cook, *Proc. R.S.* A, **115**, 334 (1927).

[†] J. E. Lennard-Jones, chap. x of *Statistical Mechanics*, by R. H. Fowler (Camb. Univ. Press, 1929).

[‡] The author gratefully acknowledges the help of Miss M. J. Littleton (H. H. Wills, Physical Laboratory, Bristol) in the numerical calculations.

[§] J. E. Lennard-Jones, chap. x of *Statistical Mechanics* by R. H. Fowler (Camb. Univ. Press, 1929).

[‖] G. P. Nijhoff, *Dissert.* (Leiden, 1928).

[¶] C. W. Gibby, C. C. Tanner and I. Masson, *Proc. R.S.* A, **122**, 283 (1929).

Table 1. Calculated force constants of gases from equation of state

		$\lambda_{(\text{rep.})}$	$\lambda_{(\text{att.})}$	Calculated closest distance in crystal (A.U.)	Calculated heat of sublimation at abs. zero in cals/gm. mol.	Observed crystal spacing	Observed heat of sublimation*
Helium	$n = 10$	$4{\cdot}38 . 10^{-82}$	$13{\cdot}8 . 10^{-60}$	3·02	106	—	—
	$n = 11$	$8{\cdot}94 . 10^{-90}$	$10{\cdot}3 . 10^{-60}$	2·93	114	—	—
	$n = 13$	$4{\cdot}55 . 10^{-105}$	$7{\cdot}43 . 10^{-60}$	2·83	126	—	—
Neon	$n = 10$	$2{\cdot}94 . 10^{-81}$	$8{\cdot}22 . 10^{-59}$	3·14	499	3·20†	590
	$n = 11$	$6{\cdot}285 . 10^{-89}$	$6{\cdot}22 . 10^{-59}$	3·04	542		
	$n = 13$	$4{\cdot}36 . 10^{-104}$	$5{\cdot}07 . 10^{-59}$	2·99	612		
Argon	$n = 10$	$7{\cdot}19 . 10^{-80}$	$10{\cdot}5 . 10^{-58}$	3·90	1730	3·84	2030
	$n = 11$	$2{\cdot}10 . 10^{-87}$	$8{\cdot}32 . 10^{-58}$	3·83	1847		
	$n = 13$	$2{\cdot}13 . 10^{-102}$	$6{\cdot}50 . 10^{-58}$	3·74	2030		
Hydrogen	$n = 10$	$4{\cdot}59 . 10^{-81}$	$1{\cdot}07 . 10^{-58}$	3·33	450	—	—
	$n = 11$	$1{\cdot}16 . 10^{-88}$	$0{\cdot}85 . 10^{-58}$	3·28	478	—	—
	$n = 13$	$7{\cdot}79 . 10^{-104}$	$0{\cdot}63 . 10^{-58}$	3·18	529	—	—
Nitrogen	$n = 10$	$1{\cdot}19 . 10^{-79}$	$13{\cdot}6 . 10^{-58}$	4·23	1380	4·0‡	1860
	$n = 11$	$3{\cdot}93 . 10^{-87}$	$11{\cdot}1 . 10^{-58}$	4·17	1460		
	$n = 13$	$4{\cdot}44 . 10^{-102}$	$8{\cdot}38 . 10^{-58}$	4·06	1640		

as it is the cubic form of least potential energy§. Argon‖ and neon¶ have already been shown experimentally to exist in this form. The calculated values of the heat of sublimation at absolute zero from this crystal structure are also given. The force constants of neon are a little uncertain because the experimental results of Holborn and Otto and those of Cath and Kamerlingh Onnes are not very consistent. The figures given are obtained by taking both sets of experimental points and adjusting the theoretical curves to fit as well as possible. Figure 3 shows the curves of potential energy of pairs of inert gas atoms as a function of their distance apart for the model $n = 13$, $m = 7$.

It is probable that many other gases are held together in the liquid and solid state by van der Waals forces, for, as London** has pointed out, many cases are known where the heat of sublimation is of the same order of magnitude as those given in the above table. CH_4, HCl, HBr, CO may be quoted as examples. Forces of this type are probably responsible also in certain cases for the adsorption of gases on solid surfaces. The author has shown that the order of magnitude of certain observed heats of adsorption can be explained in this way*. Other cases have been worked out recently by London†.

---

* For reference see F. London, *Zeit. f. phys. Chem.* **11**, 240 (1930).

† J. de Smedt, W. H. Keesom and H. H. Mooy, *Proc. Amst. Acad.* **33**, 255–257 (1930).

‡ Vegard, *Nature*, **124**, 267, 337 (1929), molecules being regarded as spheres.

§ J. E.. Lennard-Jones and A. E. Ingham, *Proc. R.S.* A, **107**, 636 (1925).

‖ F. Simon u. C. Simson, *Zeit. f. Phys.* **25**, 160 (1924).

¶ J. de Smedt, W. H. Keesom and H. H. Mooy, *loc. cit.*

** F. London, *Zeit. f. phys. Chem. loc. cit.*

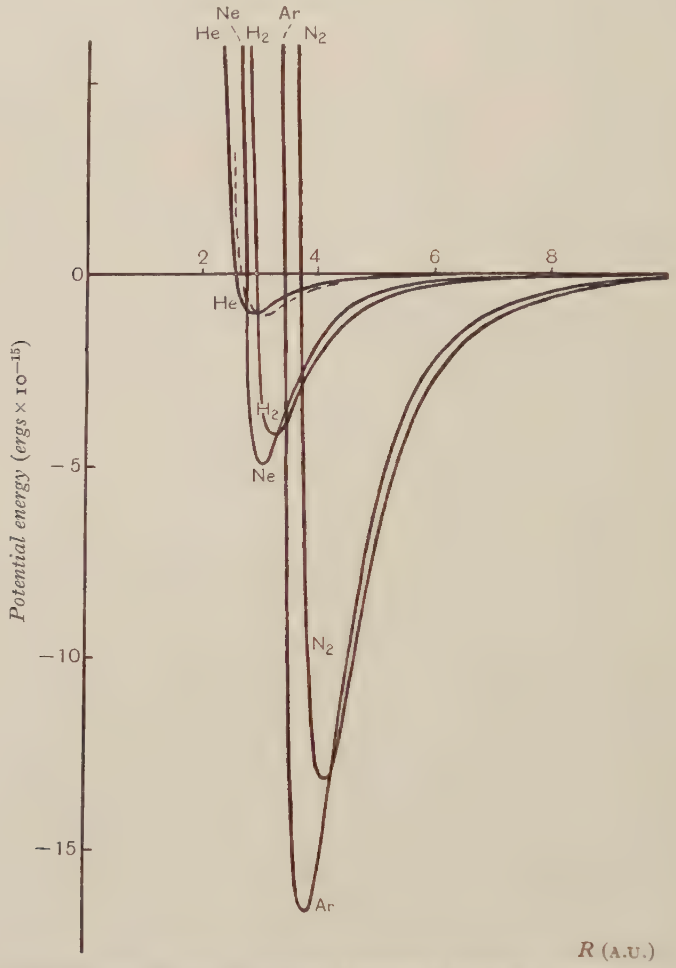


Fig. 3. The potential energy of pairs of inert gas atoms as a function of their distance apart in A.‡

The experimental study of molecular spectra has established the existence of molecules such as HgAr, HgKr§, and lately it has been shown that a molecular form of K_2 exists quite other than the molecule formed by the usual homopolar forces‖. There is little doubt that these molecules are held together by van der Waals forces.

---

* J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* **24**, 92 (1928).

† F. London, *Zeit. f. phys. Chem. loc. cit.*

‡ The continuous curves are obtained from the equation of state, hitherto unpublished, assuming a law of force $\lambda_{(\text{rep.})} R^{-13} - \lambda_{(\text{att.})} R^{-7}$. The dotted curve for helium is obtained by Slater and Kirkwood from its electronic structure.

§ O. Oldenburg, *Zeit. f. Phys.* **55**, 1 (1929).

‖ H. Kuhn, *Naturwissen.* **18**, 332 (1930).

§ 8. HOMOPOLAR COHESION*

In an earlier paragraph we have seen that when there are several electrons in an atom, its configuration may in an approximate theory be specified by a number of wave functions $u_1, u_2 \dots u_N$, each a function of the four coordinates of an electron, and that the probability of a specified configuration of the electrons is given by a certain determinant of N rows and columns. The importance of the new form for the probability function becomes evident when calculations are made of the *energy* of electronic systems. The average value of the electrostatic energy of the electrons can be calculated only when we know the probability that any pair of electrons will be at a specified distance apart. A detailed calculation of the energy of an atom or the interaction energy of two atoms depends then very closely on the probability function $\Psi\bar{\Psi}$.

The probability of finding two electrons in specified places $d\tau_1$ and $d\tau_2$, independently of the position of the other electrons, is obtained by integrating the probability function over the coordinates of all the electrons except two. The result proves to be

$$\{\rho(1, 1)\,\rho(2, 2) - \rho(1, 2)\,\rho(2, 1)\}\,d\tau_1\,d\tau_2,$$

with the definitions of $\rho(1, 2)$, etc., given in § 3. The mutual potential of two electrons consists then of two terms; the first is the average of $(e^2/r_{12})\,\rho(1, 1)\,\rho(2, 2)$ integrated over the whole of space of electrons 1 and 2; the second is the average of $(e^2/r)\,\rho(1, 2)\,\rho(2, 1)$. Apart from certain terms of these expressions which cancel, the first represents the Coulomb interaction of the individual distributions of electric charge $u_1\bar{u}_1$, $u_2\bar{u}_2$, etc. This may be called the *Coulomb energy*. It is the mutual electrostatic potential energy of the superimposed patterns which go to make up atoms, as described in § 4.

The second term in the above expression is new. It is difficult to describe its physical nature. All that can be said of it is that it is the natural outcome of the introduction of two new physical concepts into the mathematical scheme, viz., the principle of the identity of electrons, and the exclusion principle of Pauli. It is sometimes described as the "exchange" term and the term in the energy expression arising from it as the "*exchange*" *energy*.

The "exchange" energy depends on the spin of the electrons, while the Coulomb energy does not. It is this property of the exchange term which has made it of so much importance in the theory of atoms and molecules. In a two-electron system, as in an excited helium atom, for instance, the electrons may have the same or opposite spins, and, owing to the exchange term, the energies of the states with the same spins are lower in every case than those of the corresponding states with opposite spin. The hydrogen molecule is another two-electron system, and here the energy is lowest when the electrons have opposite spin. This appears to be the case in the interaction of most atoms. For certain interatomic distances the energy is lowest, and, therefore, the cohesion greatest, when the electrons of one atom are "paired" with those of the other atom. The energy of two interacting nitrogen atoms is highest when the spins of the three outer electrons of the atoms are all of them the same, and lowest when the three electrons of one atom are paired with those of the other. This latter condition corresponds to the normal nitrogen molecule, held together—as the chemist describes it—with a triple bond.

---

* The account of homopolar forces given here is necessarily brief. A fuller account has been given recently by the author in a lecture to the London Mathematical Society on "The Quantum Mechanics of Atoms and Molecules." This is to be published in the *Journal of the London Mathematical Society* shortly.

The pairing of electrons is thus brought into close connexion with the valency rules of the chemist, and chemical homopolar forces are elucidated to this extent—that they are seen to be a consequence of the same mathematical and physical principles which have been formulated for other branches of physics. This result may conceivably come to be regarded as one of the greatest achievements of the present formulation of quantum mechanics.

The nature of these forces may be described in a simpler but less accurate way by an appeal to Pauli's exclusion principle. For one electron in the field of two nuclei, there is a set of patterns with different energies just as there is for an electron in the field of one nucleus. One electron in the presence of two hydrogen nuclei will take up the pattern of lowest energy. If a second electron is added to the system, it also can take up the same pattern provided that it has a spin, which is opposite from the first one. The two electrons now exist in the same *molecular* pattern and are paired. Provided the energy of the pattern, which depends on the internuclear distance, has a minimum, a stable molecule will be formed.

If, however, two helium atoms are brought together the electrons are paired already. When the nuclei are pushed together, two of the electrons must be "promoted" to a higher energy level if the exclusion principle is to be preserved. The act of promotion requires energy and this appears as repulsion. A similar argument may be used for other closed electron groups, which are brought into contact.

The more accurate method described above also shows that closed electron groups, like those of the inert gases, repel each other. The exchange term in this case becomes predominant and leads to an increase of energy as the two systems are brought near together. *Intrinsic repulsive* fields may be attributed to this new exchange term, which quantum mechanics has produced.

The exchange term is more important than the Coulomb term in the interaction of two hydrogen atoms, but the Coulomb term becomes relatively more and more important in the interaction of larger atoms. This is due not only to the increased spread of the atoms, but also to the form of the patterns which the outer electrons have to assume. The effect is found even in the interaction of two lithium atoms*. When the Coulomb part is important, the pictures of atoms given in an earlier paragraph are useful in constructing models of molecules and helpful in understanding their various shapes. We have, for instance, seen that an atom of fluorine, or indeed any halogen gas, has a "hole" in it. It follows that the nucleus is less screened in some directions than others. If the hole in the F atom is like the (2, 1, 0) pattern, the atom is roughly like a spherical ball of electric charge with a double conical hole scooped out of it. It is then not difficult to understand why a hydrogen atom can combine with it to give a HF molecule. The hydrogen's electron cloud sinks as far as possible into the hole of the fluorine, for in this position it gets as near as possible to the fluorine nucleus. Of course, it must be stressed that this only provides a rough picture. In an accurate treatment, the wave function of the whole system must be considered.

---

* M. Delbrück, *Ann. d. Phys.* 5, 36 (1930).

§ 9. IONIC COHESION

The conception of a halogen atom as an inert gas atom with a hole in it is useful in many ways. It has an affinity for another electron, and when one has been secured the electron cloud becomes spherically symmetrical. Ionic salts, like NaCl, may be pictured as arrays of spherical distributions, each on the whole charged, either positively or negatively, and so held together by electrostatic forces. This brings us to the question of determining a criterion between homopolar cohesion and ionic cohesion. When are we to suppose that atoms become ionized in the process of binding? The criterion is one of energy. Suppose that in figure 4 the curve (1) refers to the energy of two neutral atoms at various distances apart and that curve (2) refers to that of the corresponding ions. The difference between the energies (1) and (2) at infinite distance is equal to the difference of the ionization potential of one atom (say an alkali) and the electron affinity of the other (say a halogen). The curve (2) is then represented by $(a - b/R)$ because of the electrostatic attraction.

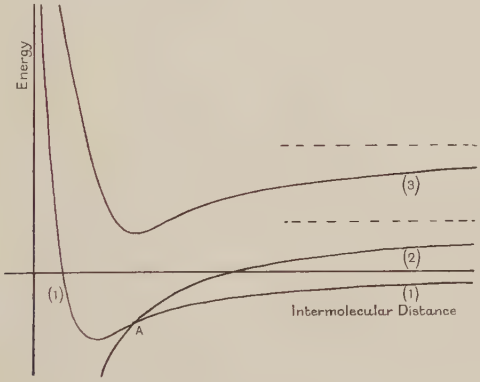


Fig. 4. Potential energy curves of atoms and ions.

At the point of intersection A of the curves, the work put into the system at infinity has been recovered, and at interatomic distances less than this the ionic form has the less energy. If, however, the energy required for ionization is large, the interaction is of the type (3). Then the ions have to be brought to very close distances before the ionic form has less energy than the atomic, but the close distances are not possible because of the intrinsic repulsion or the Pauli principle referred to in the preceding paragraph.

Table 2* shows how this condition is fulfilled in the case of some typical ionic compounds. The distance *R* refers to the value of the abscissa where the ionic curve cuts the axis; this is approximately the same as the place where it cuts the curve (1) when *R* is large.

Table 2.

	Ionization potential + electron affinity (volts)	(Å.U.)
KF	0·24	60
KCl	0·50	29
KBr	0·84	17
KI	1·23	11·8

It is likely that the terms *ionic* and *homopolar* refer to extreme cases, convenient for classification, but rarely existing in practice, actual cohesion being neither the one nor the other but partaking of both. The wave function of a perturbed system must be expressed in terms of all the wave functions of the unperturbed system and if there are two such wave functions of nearly the same energy, the wave function of the molecule is a linear function of both.

§ 10. METALLIC COHESION

From the point of view of wave mechanics, a metal must be regarded as an enormous molecule, with an enormous number of energy levels and electron patterns. The problem is to explain why a collection of atoms in the form of a metal has less energy than the isolated atoms of which it is composed. Is the cohesion due to ordinary electrostatic forces or to the exchange phenomenon or both? The problem has been considered recently in a qualitative way by J. C. Slater†, who has shown that it is likely that atoms of one spin are surrounded by others of opposite spin‡. In those metals, which are of the body-centred-cubic type of structure, each atom is at the centre of eight others of opposite electron spin.

In the bringing of the atoms together in this way the patterns of the individual atoms have been made to overlap. An electron which formerly belonged to one nucleus is now brought under the influence of several. This has the effect of increasing the electrostatic attraction, and even in the absence of any other cohesive force the metal would hold together. The metal is like a sea of electric fluid, in which the nuclei float like buoys.

---

* This method of illustration is due to F. London, *Zeit. f. Phys.* **46**, 475 (1928).

† J. C. Slater, *Phys. Rev.* **35**, 509 (1930).

‡ This is not true, of course, for the ferromagnetic bodies.

Now we inquire how the exchange phenomenon affects the cohesion. It is not difficult to show that the state of a crystal, in which all the electron spins are perfectly paired, combines only with the states in which two of the spins are interchanged. Thus, to use a linear example, the electron spins being denoted by α and β, the state $\alpha\beta\ \alpha\beta\ \alpha\beta\ldots$ combines only with $\alpha\beta\ \beta\alpha\ \alpha\beta\ldots$ and similar arrays. In the body-centred-cubic lattice the effect of such an interchange is to surround two electrons with seven neighbours of the same spin. The resulting structure has then considerably higher energy, because the contiguity of like spins causes a repulsion. It is thus highly improbable. The electron seems to know what will be the result of an interchange and decides that it simply is not done—or at any rate only with moderation. The net result is that the exchange effect is not as important in metals as it is in diatomic molecules, whereas the electrostatic attraction is relatively more important. An accurate quantitative treatment of the problem is, however, still required.

There are some metals, such as zinc and cadmium, in which the exchange term probably makes little or no contribution to the cohesion. The atoms of which they are composed have paired electron spins even when widely separated, and may be expected on that account to repel like inert-gas atoms when brought into contact. The fact that the metals are diamagnetic is further evidence that the metals consist of perfectly paired electron spins and are formed from normal unexcited atoms. Now the diatomic molecules Zn_2, Cd_2, are known to exist and the order of magnitude of their heats of dissociation, which is known from molecular spectra, suggests that these molecules are held together by van der Waals fields. The cohesion of the corresponding metals is several times greater, but this is probably due to the larger number of immediate neighbours and the additive property of van der Waals fields. Thus it seems likely that van der Waals fields make a greater contribution to the cohesion of some metals than has yet been realized.

Metallic cohesion cannot therefore be classified in any simple way. It is probably due partly to the electrostatic interaction of space-charge distributions, partly to the exchange phenomenon, and partly to van der Waals fields. The relative extents to which these various factors contribute to the cohesion of a metal must vary from case to case and is still a matter for investigation.

§ 11. CONCLUSION

In conclusion we may summarize the contributions of the new quantum mechanics to this branch of physics under four headings:

(1) It has provided density pictures of atoms which have permitted the evaluation of the electrostatic interaction of atoms in a way quite impossible in an orbital theory.

(2) It has led to the introduction of a new concept —an exchange force, which is responsible for the homopolar bonds of the chemist.

(3) It has provided pictures of asymmetrical atoms like the halogens and thrown light on the nature of electron affinity. This affinity is responsible for ionic structures of the NaCl type.

(4) It has provided an explanation of van der Waals fields, which formerly were not understood.

The general principles seem to be established. What is now required is a mathematical technique capable of applying them to particular cases.

THE ABSORPTION AND DISSOCIATIVE OR IONIZING EFFECT OF MONOCHROMATIC RADIATION IN AN ATMOSPHERE ON A ROTATING EARTH

PART II. GRAZING INCIDENCE

By S. CHAPMAN, M.A., D.Sc., F.R.S.

Received March 28, 1931. *Read June* 4, 1931.

ABSTRACT. The absorption of radiation from the sun in an atmosphere varying exponentially with the height is considered, as in a former paper; but here the earth's curvature, and that of the level layers in the atmosphere, is taken into account. The values of this absorption as previously calculated are valid so long as the sun's zenith distance does not exceed 75°, but for greater zenith distances the necessary corrections are of importance. It is shown that the absorption, and resulting ionization or dissociation of the air, should begin to increase before ground sunrise, the interval varying from about 10 minutes at the equator to about an hour at 60° latitude.

§ 1. INTRODUCTION

THIS paper is a sequel to one* with the same (main) title, which will here be referred to as part I. In § 4 of that paper, dealing with the absorption of radiation, it was pointed out that the equation of absorption there used was not mathematically exact (except for direct incidence) as a representation of the physical assumptions adopted at the outset; it was suggested that the approximation was probably sufficiently accurate for beams inclined to the vertical at angles up to 85°, but that for greater angles, corresponding to nearly grazing incidence, the error became appreciable. It was further stated that the values of the ion-content deduced in the paper were very nearly true, in low latitudes, except near dawn, but that in higher latitudes, *in winter*, the necessary corrections are appreciable up to noon. In the present paper the absorption of radiation at nearly grazing incidence is considered in detail, and the consequent corrections to the former results, relating to the variation of ion-content with respect to height and time, are examined.

The notation of part I will in general be used in this paper without being re-defined. The tables and diagrams in this paper are numbered in continuation of those of part I.

§ 2. THE ABSORPTION OF RADIATION

In considering the absorption of radiation we shall ignore the refraction of the beam; that is, the radiation will be regarded as travelling along a straight line.

In figure 18 let O denote the earth's centre, OS the line from O to the sun, P' any point in the earth's atmosphere, and NTM part of the boundary of the section of the earth by the plane SOP'; N is thus the point on the earth immediately "below" the sun, and M the antipodal point. T is a point on the "twilight circle" of the earth, dividing the day hemisphere, from which the sun is visible, from the night hemisphere.

---

* S. Chapman, *Proc. Phys. Soc.* **43**, 26 (1931).

λ
s
a, h', p

The flow of radiation is parallel to SO, and if $\angle\ SOP' = \lambda$, the angle of incidence of the beam at P' is λ. Let the beam through P' cut OT in T', and let distance s along the beam be measured from T' as origin, in the direction of travel of the beam. If a denotes the radius of the earth, and h' the height of P', then p, representing the distance from O of the beam through P', is given by

$$p = OT' = (a + h') \sin \lambda \qquad \text{......(1).}$$

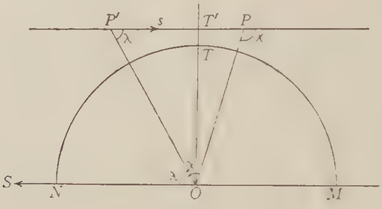


Fig. 18.

Along any particular beam p is constant, while for different points P' along it, specified by the corresponding angle λ, the height h' is given by

$$h' = p \operatorname{cosec} \lambda - a \qquad \text{......(2).}$$

For the value of s at P' we have

$$s = -p \cot \lambda \qquad \text{......(3);}$$

this is negative if P' is to the left of OT (as in figure 18) and positive if to the right.

ρ', S'

Consider the absorption $-dS'$ between the point P' and a neighbouring point on the beam, given by $s + ds$ or $\lambda + d\lambda$. If ρ' is the air density at P', and S' the intensity of radiation,

$$\begin{aligned} dS' &= -AS'\rho' ds \\ &= -AS'\rho_0 \exp(-h/H)\, p \operatorname{cosec}^2 \lambda\, d\lambda \\ &= -AS'\rho_0 \exp\{(a - p \operatorname{cosec} \lambda)/h\}\, p \operatorname{cosec}^2 \lambda\, d\lambda \qquad \text{......(4).} \end{aligned}$$

χ
S

Let P be any point on the beam, such that $\angle\ SOP = \chi$; in figure 18 this point is shown to the right of OT, but it may be anywhere along the beam. The intensity S of the beam, at P, is obtainable by integration along it from the extreme left, outside the atmosphere (where $s = -\infty$, $\lambda = 0$) to P. We get

$$S/S_\infty = \exp\left[-A\rho_0 \int_0^\chi \exp\{(a - p \operatorname{cosec} \lambda)/H\}\, p \operatorname{cosec}^2 \lambda\, d\lambda\right] \qquad \text{......(5).}$$

This equation replaces equation (7) of part I, which is not strictly true for an atmosphere arranged in concentric spherical layers of equal density.

The absorption of radiation per cm.^{3} of atmosphere is $-dS/ds$; we shall consider, instead of this, the quantity $I \equiv -\beta dS/ds$, where β denotes the number of ions produced by the absorption of unit quantity of the radiation (or the number of molecules dissociated, when the effect of the radiation is dissociative rather than ionizing). By putting $\beta = 1$ in I we can obtain the actual absorption if required.

I, β

From (4) the value of I at P is found, on substituting for S from (5), to be given by

$$I = \beta A S_\infty \rho_0 \exp(-h/H) \exp\left[-A\rho_0 \int_0^\chi \exp\{(a - p \operatorname{cosec} \lambda)/H\} p \operatorname{cosec}^2 \lambda \, d\lambda\right] \qquad \text{......(6).}$$

In terms of I_0 ($\equiv \beta S_\infty / H \exp 1$) and h_0 (given by $\exp(h_0/H) = A\rho_0 H$) this may be written

I_0, h_0

$$\frac{I}{I_0} = \exp\left(1 + \frac{h_0 - h}{H}\right) \exp\left[-\frac{p}{H}\int_0^\chi \exp\left(\frac{a + h_0 - p \operatorname{cosec} \lambda}{H}\right) \operatorname{cosec}^2 \lambda \, d\lambda\right], \qquad \text{......(7)}$$

or, taking $z \equiv (h - h_0)/H$, as in part I, and substituting $(a + h) \sin\chi$ or $(a + h_0 + zH) \sin\chi$ for p,

$$\frac{I}{I_0} = \exp\left[1 - z - \left(\frac{a + h_0}{H} + z\right) \sin\chi \int_0^\chi \exp\left\{\frac{a + h_0}{H} - \left(\frac{a + h_0}{H} + z\right)\frac{\sin\chi}{\sin\lambda}\right\} \operatorname{cosec}^2 \lambda \, d\lambda\right] \qquad \text{......(8).}$$

This equation replaces (14) or (17) in part I, and differs from those equations in one important respect; it contains a quantity $(a + h_0)/H$ which did not occur in the former discussion. Thus the proper consideration of the earth's curvature involves the introduction of a new parameter into the formulae, and if for no other reason than this it seemed justifiable, in a first general discussion of the subject, to defer the consideration of the curvature, particularly since this made it possible to put the analysis in a very general form involving only one parameter (σ_0).

The further parameter now introduced, $(a + h_0)/H$, is equal to the distance, *expressed in terms of H as unit of length*, from the earth's centre to the level at which, at noon at the equator, the absorption of radiation is a maximum. This parameter will be denoted by R.

R

It is of interest to consider the numerical value of R in the case of the ionized layers of which the heights have been measured by E. V. Appleton and his collaborators*. The value of a is 6370 km. For the lower of the observed ionized layers h_0 is about 100 km., which is small, though not negligibly so, compared with a; thus $a + h_0$ is about 6470 km. for this layer. The value of H at this height in the atmosphere is unknown; if the temperature there is 300° K. and the composition is the same as in the lower atmosphere, $H = 8 \cdot 4$ km. It is possible that H may vary with the season, and even throughout the day and night; temperatures as high as 1000° K. have been suggested as existing at great heights, and for the same composition as before this would correspond to $H = 28$ km. At great heights (probably much above 100 km.) the composition is likely to differ considerably from that near the ground, and I have suggested elsewhere* that in the outermost layer atomic oxygen and nitrogen, possibly ionized, may be the main constituents; if so, at these heights H would be increased, on this account, in the ratio 2 (if the atoms are not ionized) or 4 (if wholly ionized, the negative charges being electrons). Thus for very high levels values of H as large as 112 km. might require consideration. The range of R or $(a + h_0)/H$, as H ranges from 8·4 to 112 km., is from about 770 to 58, if $h_0 = 100$, or slightly more for higher values of h_0. It is convenient, in the subsequent calculations, to bear in mind this possible extreme range of the new parameter R; but for the ionized layer at about 100 km. height, H is probably about 10 km., corresponding to R about 647 or, in round figures, 650.

---

* E. V. Appleton, *Proc. R.S.* A, **126**, 542 (1930); *ibid.* **128**, 133 and 159 (1930), with J. A. Ratcliffe and A. L. Green respectively; and earlier papers there cited.

In terms of R, (8) may be written

$$I/I_0 = \exp\left[1 - z - \exp(-z)\, f(R + z, \chi)\right] \qquad \text{......(9)},$$

where

$$f(x, \chi) = x \sin\chi \int_0^{\chi} \exp\{x(1 - \sin\chi/\sin\lambda)\} \operatorname{cosec}^2\lambda \, d\lambda \qquad \text{......(10)}.$$

Equation (9) is identical with equation (17) of part I, except that in (17) $\sec\chi$ occurs in the place of $f(R + z, \chi)$. It is of interest to show that $f(R + z, \chi)$ actually has the value $\sec\chi$ when R tends to infinity, because of course the neglect of the earth's curvature, in part 1, corresponds to taking R (or $R + z$) as infinite.

Since

$$d \operatorname{cosec}\lambda = -\cos\lambda \operatorname{cosec}^2\lambda \, d\lambda,$$

(10) may be rewritten as

$$f(x, \chi) = \int_{\lambda=0}^{\lambda=\chi} \sec\lambda \, d\left[\exp\{x(1 - \sin\chi \operatorname{cosec}\lambda)\}\right] \qquad \text{......(11)},$$

and, by a partial integration, this gives

$$\begin{aligned} f(x, \chi) &= \Big[\sec\lambda \exp\{x(1 - \sin\chi \operatorname{cosec}\lambda)\}\Big]_{\lambda=0}^{\lambda=\chi} \\ &\qquad - \int_0^{\chi} \exp\{x(1 - \sin\chi \operatorname{cosec}\lambda)\} \sec\lambda \tan\lambda \, d\lambda \\ &= \sec\chi - \int_0^{\chi} \exp\{x(1 - \sin\chi \operatorname{cosec}\lambda)\} \sec\lambda \tan\lambda \, d\lambda \qquad \text{......(12)}. \end{aligned}$$

It is not difficult to prove that as $x \to \infty$ the second term in the last line of (12) tends to zero provided that χ is less than 90°; such values were the only ones that came in question in the former paper. Thus when R is taken as infinite, as was done there, $f(x, \chi)$ is equal to $\sec\chi$. The revised discussion in the present paper depends essentially on the replacement of $\sec\chi$ in equation (17) of part 1 by $f(R + z, \chi)$ as here defined, and it is necessary to consider the nature of this function of the two variables x (or $R + z$) and χ.

It should be added that for any beam for which values of χ exceeding 90° have to be considered, p cannot be less than a, the radius of the solid body of the earth.

---

* *Phil. Mag.* **10**, 369 (1930).

This imposes an upper limit on the possible values of χ for any height h, since $p \geqslant a$ is equivalent to $(a+h)\sin\chi \geqslant a$. For example, for $h = 100$ km., the limiting value of χ is about 100°. This restriction has little actual importance, however, for the problem of upper atmospheric ionization, because the absorption of the beams for which p only slightly exceeds a is practically completed well before the limiting value of χ is attained.

§ 3. THE FUNCTION $f(x, \chi)$ WHEN $\chi = \frac{1}{2}\pi$

When $\chi = \frac{1}{2}\pi$, $\sec\chi$ is infinite, whereas $f(x, \chi)$ is finite; this infinity of $\sec\chi$ in (17) renders I zero, corresponding to complete absorption of radiation by the time the beam reaches the twilight plane (i.e. the plane through O perpendicular to SO). Actually the value of I is still positive on reaching this plane, and also for points "behind" this plane, corresponding to values of χ greater than $\frac{1}{2}\pi$.

For the special value $\chi = \frac{1}{2}\pi$, $f(x, \chi)$ may be expressed in terms of Bessel functions. For

$$f(x, \tfrac{1}{2}\pi) = x\int_0^{\frac{1}{2}\pi} \exp\{x(1-\operatorname{cosec}\lambda)\}\operatorname{cosec}^2\lambda\, d\lambda \qquad \text{......(13).}$$

On making the substitution $\sin\lambda = \operatorname{sech} u$ ......(14),

so that

$$\left.\begin{aligned} \cos\lambda &= \tanh u, & \tan\lambda &= \operatorname{cosech} u \\ \sec\lambda &= \cosh u, & \sec\lambda &= \coth u \\ \cot\lambda &= \sinh u, & d\lambda &= -\operatorname{sech} u\, du \end{aligned}\right\} \qquad \text{......(15),}$$

we find that (13) becomes

$$\begin{aligned} f(x, \tfrac{1}{2}\pi) &= x\int_0^\infty e^{x(1-\cosh u)}\cosh u\, du \\ &= -xe^x \frac{d}{dx}\int_0^\infty e^{-x\cosh u}\, du \\ &= -xe^x \frac{d}{dx} K_0(x) = -xe^x K_1(x) \qquad \text{......(16),} \end{aligned}$$

by well-known formulae in the theory of Bessel functions*. Tables of the function $e^x K_1(x)$ up to $x = 16$ are given at the end of Watson's treatise on these functions.

Since in the present application x is large (50 or more), the well-known asymptotic formula for $K_1(x)$ may be used, which gives

$$f(x, \tfrac{1}{2}\pi) = (\tfrac{1}{2}\pi x)^{\frac{1}{2}}\left\{1 + \sum_{n=1} a_n x^{-n}\right\} \qquad \text{......(17),}$$

where $a_n = [\{1.3\ldots(2n-3)\}^2(4n^2-1)]/(n!\,2^{3n})$ ......(18),

so that $a_1 = \frac{3}{8}$, $a_2 = -\frac{15}{128}$, $a_3 = \frac{105}{1024}$, ...(19).

Thus for $x > 50$, $f(x, \frac{1}{2}\pi) = (\frac{1}{2}\pi x)^{\frac{1}{2}}$ correct to within 1 per cent. For $x = 50$ it is 8·93, while for $x = 800$ it is 35·47; these values replace infinity, the value of $\sec\chi$, when (9) replaces (17) of part I.

---

* Cf. Whittaker and Watson, *Modern Analysis* (2nd ed.), p. 377, ex. 40.

§4. THE FUNCTION $f(x, \chi)$ FOR SMALL VALUES OF χ

The smaller the value of χ, the more nearly will $f(x, \chi)$ approximate to $\sec\chi$, so that for small values of χ a formula expressing this fact should be obtainable. It may be found as follows. Let

y

$$y = x \sin\chi \qquad \text{......(20)},$$

so that

$$f(x, \chi) = ye^{x} \int_0^{\chi} e^{-y \operatorname{cosec} \lambda} \operatorname{cosec}^2 \lambda \, d\lambda$$

$$= - e^{x} \int_{\lambda=0}^{\lambda=\chi} \sec\lambda \, d\left(e^{-y \operatorname{cosec}\lambda}\right)$$

$$= \sec\chi - e^{x} \int_0^{\chi} e^{-y \operatorname{cosec}\lambda} \sec^2\lambda \sin\lambda \, d\lambda$$

$$= \sec\chi - (e^{x}/y) \int_{\lambda=0}^{\lambda=\chi} \tan^3\lambda \, d\left(e^{-y \operatorname{cosec}\lambda}\right) \qquad \text{......(21)},$$

by a partial integration similar to that which we used in obtaining (12). By further similar partial integrations we find that

$$f(x, \chi) = \sec\chi + \sum_{n=1} b_n/x^n \qquad \text{......(22)},$$

where

$$\left.\begin{aligned} &b_1 = -\sec\chi\tan^2\chi, \quad b_2 = 3\tan^2\chi\sec^3\chi, \quad b_3 = -(15\tan^4\chi + 12\tan^2\chi)\sec^3\chi \\ &b_4 = (105\tan^4\chi + 60\tan^2\chi)\sec^5\chi, \\ &b_5 = -(945\tan^6\chi + 1260\tan^4\chi + 360\tan^2\chi)\sec^5\chi \end{aligned}\right\} \qquad \text{......(23)},$$

and, in general,

$$b_n \sin^n\chi = -\sin^2\chi\sec\chi\,(d/d\chi)\,(b_{n-1}\sin^{n-1}\chi) \qquad \text{......(24)}.$$

This series is useful only so long as $(\tan^2\chi)/x$ is small; for $x = 800$ it is of service for values of χ up to about 80°, but for $x = 50$ its numerical convergence becomes slow at $\chi = 60°$. The following table gives values of the *ratio* $100\{1 - f(x, \chi)/\sec\chi\}$, calculated (except for $\chi = 75°$ and $R \leqslant 200$) in the above way for various values of R and χ; this indicates the *percentage* by which f falls short of $\sec\chi$ in the various cases.

Table 3. $100\{1 - f(x, \chi)/\sec\chi\}$

$\chi =$	30°	45°	60°	75°
$\sec\chi =$	1·155	1·414	2·000	3·864
$R =$ 50	0·62	1·2	4·6	16·4
100	0·32	0·95	2·7	9·1
200	0·16	0·49	1·4	5·6
300	0·11	0·32	1·0	4·1
400	0·08	0·23	0·7	3·2
500	0·06	0·20	0·6	2·6
600	0·05	0·16	0·5	2·2
650	0·05	0·15	0·5	2·0
700	0·05	0·14	0·4	1·9
800	0·04	0·13	0·4	1·7

It is clear from this table that if $R > 300$ (corresponding to $H < 20$ km. approximately), the curvature of the earth reduces the factor $\sec\chi$ of part 1, equations (8), (9), (12), (14), (17), by less than 5 per cent., even when χ is as large as 75°.

§ 5. GENERAL ASYMPTOTIC FORMULAE FOR $f(x, \chi)$

When χ is neither small nor equal to $\frac{1}{2}\pi$, $f(x, \chi)$ may be evaluated as follows. Using the substitutions (14) and (20), we find

$$f(x, \chi) = ye^{x-y} \int_U^\infty e^{y(1-\cosh u)} \cosh u \, du \qquad \text{......(25)},$$

where U is the value of u corresponding to $\lambda = \chi$, so that U

$$\operatorname{sech} U = \sin \chi \qquad \text{......(26)}.$$

If $\chi < \frac{1}{2}\pi$, the positive value of U must be taken, but if $\chi > \frac{1}{2}\pi$, the negative value is the appropriate one. If we write

$$\chi = \tfrac{1}{2}\pi - \chi' \qquad \text{......(27)},$$ χ'

U will have the same sign as χ', or, if we take χ' and U as always positive and given by

$$\operatorname{sech} U = \cos \chi' \qquad \text{......(28)},$$

(25) may be written in the form

$$\begin{aligned} f(x, \tfrac{1}{2}\pi \mp \chi') &= ye^{x-y} \int_{\mp U}^\infty e^{y(1-\cosh u)} \cosh u \, du \\ &= ye^{x-y} \left\{ \int_0^\infty \mp \int_0^U \right\} e^{y(1-\cosh u)} \cosh u \, du \\ &= e^{x-y} f(y, \tfrac{1}{2}\pi) \mp ye^{x-y} \int_0^U e^{y(1-\cosh u)} \cosh u \, du \qquad \text{......(29)}. \end{aligned}$$

Writing $\quad v = \sinh \frac{1}{2}u, \quad \cosh u - 1 = 2v^2, \quad du = (2\, dv)/(1 + v^2)^{\frac{1}{2}} \qquad$ ......(30) v

we have

$$\begin{aligned} \int e^{y(1-\cosh u)} \cosh u \, du &= 2 \int \exp(-2yv^2) \frac{1 + 2v^2}{(1 + v^2)^{\frac{1}{2}}} \, dv \\ &= 2 \int \exp(-2yv^2)(1 + \Sigma\, c_n v^{2n}) \, dv \qquad \text{......(31)}, \end{aligned}$$

where

$$\left. \begin{aligned} c_n &= (-1)^{n-1}(2n + 1)\{1.3 \dots (2n - 3)\}/n!\, 2^n \\ c_1 &= \tfrac{3}{2}, \quad c_2 = -\tfrac{5}{8}, \quad c_3 = \tfrac{7}{16}, \quad c_4 = -\tfrac{45}{128}, \dots \end{aligned} \right\} \qquad \text{......(32)}.$$

Now it is readily shown that, for all positive values of y and V,

$$\begin{aligned} \int_0^V \exp(-2yv^2)\, v^{2n} \, dv = {} & \frac{1.3 \dots (2n - 1)}{2^{2n+\frac{1}{2}}\, y^{n+\frac{1}{2}}} \operatorname{erf}(2yV^2)^{\frac{1}{2}} \\ & - \exp(-2yV^2) \left\{ \frac{V^{2n-1}}{4y} + \frac{(2n - 1)\, V^{2n-3}}{(4y)^2} + \frac{(2n - 1)(2n - 3)\, V^{2n-5}}{(4y)^3} + \dots \right\} \\ & \qquad \text{......(33)}, \end{aligned}$$

where the series on the right is a terminating one, and where

$$\operatorname{erf} \eta = \int_0^\eta e^{-w^2} \, dw \qquad \text{......(34)}.$$ η

By well-known theorems, $\quad \dfrac{2}{\sqrt{\pi}} \operatorname{erf} \eta \to 1 \text{ as } \eta \to \infty \qquad$ ......(35), and, in the form of an asymptotic series, useful when η is large,

$$1-\frac{2}{\sqrt{\pi}}\operatorname{erf}\eta=\frac{2}{\sqrt{\pi}}\int_{\eta}^{\infty}e^{-w^2}dw=\frac{e^{-\frac{1}{2}\eta^2}}{\sqrt{(\pi\eta)}}W_{-\frac{1}{4},\frac{1}{4}}(\eta^2)$$

$$=\frac{e^{-\eta^2}}{\eta\sqrt{\pi}}\left[1+\Sigma(-1)^n\frac{1.3\ldots(2n-1)}{2^n\eta^{2n}}\right]\qquad\ldots\ldots(36),$$

V where W denotes the confluent hypergeometric function*. Hence if V is the value of v corresponding to $u=U$, it follows that

$$ye^{x-y}\int_0^U e^{y(1-\cosh u)}\cosh u\,du$$

$$=e^{x-y}(\tfrac{1}{2}\pi y)^{\frac{1}{2}}\left\{\frac{2}{\sqrt{\pi}}\operatorname{erf}(2yV^2)^{\frac{1}{2}}\right\}\left\{1+\frac{c_1}{4y}+\frac{1.3c_2}{(4y)^2}+\ldots\right\}$$

$$-\frac{1}{2}\left[\sum_1^{\infty}c_nV^{2n-1}+\frac{1}{4y}\sum_2^{\infty}(2n-1)c_nV^{2n-3}+\frac{1}{(4y)^2}\sum_3^{\infty}(2n-1)(2n-3)c_nV^{2n-5}+\ldots\right]$$

$$=-ye^xK_1(y)\frac{2}{\sqrt{\pi}}\operatorname{erf}(2yV^2)^{\frac{1}{2}}-\tfrac{1}{2}\sum_{m=0}^{\infty}(4y)^{-m}\sum_{n=m+1}^{\infty}(2n-1)(2n-3)\ldots$$

$$\ldots(2n-2m+1)c_nV^{2n-2m-1}\qquad\ldots\ldots(37).$$

Hence by (29) and (16),

$$f(x,\tfrac{1}{2}\pi\mp\chi')=-ye^xK_1(y)\left\{1\mp\frac{2}{\sqrt{\pi}}\operatorname{erf}(2yV^2)^{\frac{1}{2}}\right\}$$

$$\pm\tfrac{1}{2}\sum_{m=0}^{\infty}(4y)^{-m}\sum_{n=m+1}^{\infty}(2n-1)(2n-3)\ldots(2n-2m+1)c_nV^{2n-2m-1}\quad\ldots(38).$$

In this formula

$$\left.\begin{aligned}V&=\sinh\tfrac{1}{2}U=\sqrt{\{\tfrac{1}{2}(\operatorname{cosec}\chi-1)\}}=\sqrt{\{\tfrac{1}{2}(\sec\chi'-1)\}}\\ y&=x\sin\chi=x\cos\chi'\end{aligned}\right\}\quad\ldots\ldots(39),$$

$$(2yV^2)^{\frac{1}{2}}=\{x(1-\sin\chi)\}^{\frac{1}{2}}=\{x(1-\cos\chi')\}^{\frac{1}{2}}\qquad\ldots\ldots(40);$$

in all cases the positive square roots are to be taken.

The formula (38) is useful when χ is too great for (22) to be rapidly convergent; when χ' is positive ($\chi<90°$) and such that $(2yV^2)^{\frac{1}{2}}$ is 3 or more, the expansion (36) is helpful in evaluating (38). The binomial expansion in (31) is valid so long as $V<1$, or $\sin\chi>\frac{1}{3}$, $\chi>20°$; in calculating $f(x,\chi)$ for smaller values of χ the formulae of § 3 are available.

When χ' is positive, and x tends to infinity, the first term of $f(x,\frac{1}{2}\pi-\chi')$, in (38), may be shown, with the aid of (36), to tend to $-1/2V$. The second part of (38) tends to $\frac{1}{2}\sum_{n=1}^{\infty}c_nV^{2n-1}$, which is equal to $1/2V+\sec\chi$. Thus this expression for $f(x,\frac{1}{2}\pi-\chi')$ tends to $\sec\chi$, as it should do, when $x\to\infty$, $0<\chi'<\frac{1}{2}\pi$.

---

* Cf. Whittaker and Watson, *Modern Analysis* (2nd ed.), p. 335.

In calculating the first term of (38), use may be made either of tables of $e^{y}K_1(y)$, or of the asymptotic formula

$$-ye^{x}K_1(y) = (\tfrac{1}{2}\pi y)^{\frac{1}{2}}\, e^{x-y} \left\{ 1 + \sum_{1} a_n y^{-n} \right\}$$

$$= (\tfrac{1}{2}\pi x \sin\chi)^{\frac{1}{2}}\, e^{x(1-\sin\chi)} \left\{ 1 + \sum_{1} a_n x^{-n} \operatorname{cosec}^n \chi \right\} \quad \text{......(40).}$$

Table 4 gives values of $f(R, \chi)$ and of $\ln f(R, \chi)$ for various values of R and χ; it also gives values of $\sec\chi$ and $\ln\sec\chi$ for comparison.

When $\chi = 0$, $f(R, \chi) = \sec\chi = 1$, and $\ln\sec\chi = \ln f(R, \chi) = 0$ for all values of R.

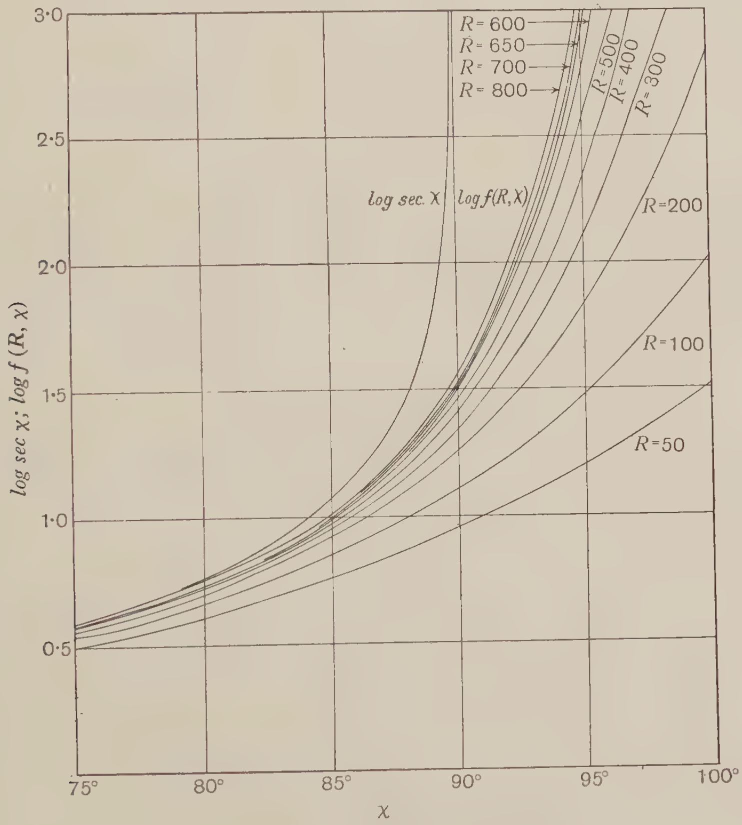


Fig. 19.

Figure 19 illustrates the functions $\log\sec\chi$ and $\log f(R, \chi)$, for various values of R, over the range of χ from 75° to 100°. If the ordinates are multiplied by 2·303, this figure also gives the values of $\ln\sec\chi$ and $\ln f(R, \chi)$.

§ 6. PROPERTIES OF THE FUNCTION $f(x, \chi)$

When $\chi < 90°$, or $\chi' > 0$, the principal factors in the first and most important term of $f(x, \chi)$, according to (38), are $e^{x(1-\sin\chi)}$ and $1 - (2/\sqrt{\pi}) \operatorname{erf} \{2yV^2\}^{\frac{1}{2}}$; the former increases as χ decreases, while the latter decreases; these tendencies approximately neutralize one another in their product, and as χ decreases from $\frac{1}{2}\pi$, $f(x, \chi)$ steadily decreases from $\sqrt{(\frac{1}{2}\pi x)}$, approximately, and tends, from below, to $\sec\chi$ for sufficiently small values of χ.

As χ *increases* from $\frac{1}{2}\pi$, the increase of $e^{x(1-\sin\chi)}$ is no longer compensated by a rapidly decreasing factor, because the factor involving $\operatorname{erf}(2yV^2)^{\frac{1}{2}}$ is now $1 + (2/\sqrt{\pi}) \operatorname{erf}(2yV^2)^{\frac{1}{2}}$, which increases from 1, when $\chi = \frac{1}{2}\pi$, and rapidly approaches the limiting value 2 when $(2yV^2)^{\frac{1}{2}}$ exceeds the value 3.

Throughout the whole range of χ, $f(x, \chi) > f(x', \chi)$, if $x > x'$.

The rate of variation of $f(x, \chi)$ with respect to χ is readily calculable:

$$\frac{\partial f(x, \chi)}{\partial \chi} = x \cos\chi \int_0^{\chi} e^{x(1-\sin\chi \operatorname{cosec}\lambda)} \operatorname{cosec}^2\lambda \, d\lambda$$
$$- x^2 \sin\chi \cos\chi \int_0^{\chi} e^{x(1-\sin\chi \operatorname{cosec}\lambda)} \operatorname{cosec}^3\lambda \, d\lambda \quad \text{......(41).}$$

This expression could, if desired, be expressed in forms similar to those derived, for suitable ranges of x and χ, in §§ 3, 4. When $\chi = \frac{1}{2}\pi$ the result is specially simple, i.e.

$$\left\{\frac{\partial f(x, \chi)}{\partial \chi}\right\}_{\chi=\frac{1}{2}\pi} = x \quad \text{......(42).}$$

The variation of $f(x, \chi)$ with respect to x is also of interest:

$$\frac{\partial f(x, \chi)}{\partial x} = \frac{x+1}{x} f(x, \chi) - x \sin^2\chi \int_0^{\chi} e^{x(1-\sin\chi \operatorname{cosec}\lambda)} \operatorname{cosec}^3\lambda \, d\lambda \quad \text{...(43).}$$

This can be evaluated by the methods adopted for $f(x, \chi)$ itself. But a general idea of the value of $\partial f/\partial x$ can be simply obtained as follows. When $\chi = \frac{1}{2}\pi$, differentiation of $(\frac{1}{2}\pi x)^{\frac{1}{2}}$, the approximate value of f (cf. § 2), gives

$$\left(\frac{\partial f}{\partial x}\right)_{\chi=\frac{1}{2}\pi} = \tfrac{1}{2}(\pi/2x)^{\frac{1}{2}} \text{ approximately} \quad \text{......(44).}$$

This is less, the greater the value of x. When $\chi = 0$, $f(x, \chi) = 1$ and $\partial f/\partial x = 0$; § 3 shows that for small values of χ the difference between $f(x, \chi)$ and $\sec\chi$ is less, the greater the value of x. This suggests that $\partial f/\partial x$ increases from 0 to approximately $\frac{1}{2}(\pi/2x)^{\frac{1}{2}}$ as χ varies from 0 to $\frac{1}{2}\pi$, being throughout smaller, the greater the value of x; this could be confirmed by a detailed discussion of (43), and is borne out by inspection of table 4. It is less easy to see how $\partial f/\partial x$ varies with x for values of χ greater than 90°, but when χ has increased sufficiently beyond $\frac{1}{2}\pi$ for the factor $1 + (2/\sqrt{\pi}) \operatorname{erf}(2yV^2)^{\frac{1}{2}}$ to have become practically 2, the principal

Table 4. Values of $f(R, \chi)$ and of $\ln f(R, \chi)$

$\chi =$	30°	45°	60°	75°	80°	83°	85°	87°	90°	93°	95°	97°	100°
$\sec \chi =$	1·155	1·414	2·000	3·864	5·758	8·206	11·474	19·107	∞				
$\ln \sec \chi$	0·1438	0·3466	0·6932	1·352	1·751	2·105	2·440	2·950	∞				
$R = 50$, $f =$	1·148	1·389	1·908	3·232	4·098	5·050	5·825	6·813	8·928	12·30	15·73	20·78	32·94
$\ln f =$	0·1377	0·3284	0·6463	1·173	1·410	1·619	1·762	1·919	2·189	2·509	2·756	3·034	3·495
$R = 100$, $f =$	1·151	1·401	1·946	3·512	4·608	5·906	7·068	8·677	12·58	20·16	29·67	49·91	106·9
$\ln f =$	0·1406	0·3370	0·6658	1·256	1·528	1·776	1·956	2·161	2·532	3·004	3·390	3·848	4·672
$R = 200$, $f =$	1·153	1·407	1·972	3·646	5·010	6·656	8·276	10·73	17·76	35·95	67·59	150·5	714·1
$\ln f =$	0·1422	0·3417	0·6788	1·294	1·611	1·895	2·113	2·373	2·877	3·582	4·214	5·014	6·571
$R = 300$, $f =$	1·153	1·410	1·981	3·706	5·281	7·020	8·918	11·96	21·74	53·57	126·9	398·2	4108
$\ln f =$	0·1427	0·3433	0·6834	1·310	1·664	1·949	2·188	2·482	3·079	3·981	4·844	5·987	8·321
$R = 400$, $f =$	1·154	1·411	1·985	3·742	5·380	—	9·327	12·82	25·09	73·94	220·1	978·4	2169×10
$\ln f =$	0·1430	0·3441	0·6858	1·320	1·683	—	2·233	2·551	3·222	4·303	5·394	6·886	9·985
$R = 500$, $f =$	1·154	1·411	1·988	3·764	5·439	—	9·620	13·48	28·05	97·92	365·6	2315	1108×10^2
$\ln f =$	0·1431	0·3446	0·6873	1·326	1·694	—	2·264	2·601	3·334	4·584	5·902	7·747	11·62
$R = 600$, $f =$	1·154	1·412	1·990	3·780	5·492	—	9·837	13·97	30·72	125·7	591·5	—	5543×10^2
$\ln f =$	0·1433	0·3449	0·6882	1·330	1·703	—	2·286	2·637	3·425	4·834	6·383	—	13·23
$R = 650$, $f =$	1·154	1·412	1·991	3·786	5·510	—	9·930	14·18	31·97	141·5	747·0	—	1233×10^3
$\ln f =$	0·1433	0·3450	0·6886	1·331	1·707	—	2·296	2·652	3·465	4·952	6·616	—	14·03
$R = 700$, $f =$	1·154	1·412	1·992	3·791	5·526	—	10·01	14·38	33·18	158·7	940·0	—	2734×10^3
$\ln f =$	0·1433	0·3452	0·6889	1·333	1·709	—	2·303	2·666	3·502	5·067	6·846	—	14·82
$R = 800$, $f =$	1·154	1·412	1·993	3·800	5·552	—	10·15	14·73	35·46	197·5	1476	—	1336×10^4
$\ln f =$	0·1434	0·3453	0·6894	1·335	1·714	—	2·317	2·690	3·569	5·286	7·297	—	16·41

factor in f, which governs the value of $\partial f/\partial x$, is $e^{x(1-\sin\chi)}$; thus $\partial f/\partial x$ is approximately equal to $(1-\sin\chi)\,f(x,\chi)$ for such values of χ. Since f increases with x, $\partial f/\partial x$ changes, between $\chi=\frac{1}{2}\pi$ and somewhat greater values, from a decreasing function of x to an increasing one. The change is completed, over the range of R here considered, before $\chi=93^\circ$, as may be seen by inspection of table 4.

§7. THE HEIGHT-DISTRIBUTION OF THE RATE OF ION-PRODUCTION

$z(\chi)$ In part I, equation (16), it was found that the value of z, written as $z(\chi)$, corresponding to the maximum value of I at a point from which the sun's zenith distance is χ, is $\ln\sec\chi$. The corresponding height $h(\chi)$ above the ground is $h_0-Hz(\chi)$;

Z if height measured from this level as datum, in terms of H as unit, be denoted by Z,

$$Z=z-z(\chi) \qquad \text{......(45)}.$$

It is of interest to point out that in terms of Z the equation (17) of part I takes a specially simple form, namely,

$$I/I_0\cos\chi=\exp\{1-Z-\exp(-Z)\} \qquad \text{......(46)}.$$

Thus the *proportionate* height-distribution of the rate of ion-production, to the accuracy afforded by the approximate formulae of part I, is the same at all points χ, relative to the *local* height of maximum ion-production; this height increases with χ to infinity at $\chi=\frac{1}{2}\pi$; the actual rate of production at points similarly situated with respect to the local level of maximum is, however, reduced, as compared with the value at the point immediately beneath the sun, in the ratio $\cos\chi$. Thus all the curves in figure 1 of part I are identical except in their scale of ordinates, and in being bodily shifted so that their maxima occur at different points along the scale of abscissae; this point was not noted in part I. The modifications in these results due to the curvature of the earth will now be considered.

The value $z(\chi)$ at which I, as given by (9), is a maximum, is given by

$$1-e^{-z}f(R+z,\chi)+e^{-z}\,\partial f(R+z,\chi)/\partial z=0 \qquad \text{......(47)}.$$

For $\chi=\frac{1}{2}\pi$ it has been seen in § 5 that $\partial f(R+z,\chi)/\partial z$ is approximately equal to $f(R+z,\chi)/2(R+z)$; thus it is negligible compared with $f(R+z,\chi)$ when $R\geqslant 50$. Consequently (47) is approximately equivalent to

$$1-\exp(-z)\,f(R+z,\chi)=0,$$

or

$$z(\chi)=\ln f(R+z,\chi) \qquad \text{......(48)}.$$

This is valid for $\chi=\frac{1}{2}\pi$, and also for smaller values, since the ratio of $\partial f/\partial z$ to f decreases with χ when $\chi<\frac{1}{2}\pi$. As $\chi\to 0$ this equation tends to the approximate equation $z(\chi)=\ln\sec\chi$ of part I.

Reckoning height from the local level of maximum I, by the substitution (45), an approximate equation analogous to (46) is obtained, namely

$$I=\{I_0/f(R+z,\chi)\}\exp\{1-Z-\exp(-Z)\} \qquad \text{......(49)}.$$

Thus the height-distribution of I, relative to the local level of maximum I, is approximately the same as at the point immediately beneath the sun (as illustrated by curve 7 in figure 1 of part I) except for a reduction, the same at all relative heights, in the ratio $1/f(R+z, \chi)$, or, in terms of $z(\chi)$, in the ratio $e^{-z(\chi)}$.

In part I, by neglect of the curvature of the earth, $z(\chi)$ was found to be infinity at $\chi = \frac{1}{2}\pi$, where I was given as zero at all heights. The earth's curvature being taken into account and the values of $f(x, \chi)$ given in table 4 utilized, it appears that $z(\frac{1}{2}\pi)$ varies from 2·18 for $R = 50$, to 3·45 for $R = 650$; thus the change of height of the level of maximum I, from the equator to the twilight circle, is only a small multiple of H. It should be remembered, however, that R itself depends on H (§ 2); h_0 being neglected in comparison with a, the earth's radius, $R = 50$ corresponds to a value of H 13 times as large as $R = 650$, so that $z(\frac{1}{2}\pi)$ for $R = 50$ represents $(2{\cdot}18 \times 13)/(3{\cdot}45)$ or 8·2 times as great a distance, in kilometres, as $z(\frac{1}{2}\pi)$ for $R = 650$. In the latter value, corresponding to $H = 10$ km., $z(\frac{1}{2}\pi)$ represents a distance of 34·5 km.

When χ increases beyond $\frac{1}{2}\pi$, the approximate expression for $\partial f(R+z, \chi)/\partial z$ changes fairly rapidly from $f/2(R+z)$ to $(1-\sin\chi) f(R+z, \chi)$, while $f(R+z, \chi)$ rapidly increases, approximately in proportion to the factor $e^{(R+z)(1-\sin\chi)}$; as $f(R+z, \chi)$ increases, I decreases; for the values of R that require consideration (§ 2), I is appreciable only so long as $1-\sin\chi$ is small, so that $\partial f(R+z, \chi)/\partial z$ in (47) is still negligible in comparison* with $f(R+z, \chi)$ over this range. Consequently (48) and (49) remain valid.

Thus, over the range for which I is appreciable, the function $f(x, \chi)$, in which x is to be given the value $R+z$, suffices to determine, in a very simple way, the level of maximum I, and the reduction of I at this and other levels above and below it, as compared with the corresponding magnitude at the point immediately beneath the sun. Since $\ln f = 2{\cdot}303 \log f$, the graphs of $\log f(R, \chi)$ in figure 19 thus indicate the variation in the *level* of maximum absorption of radiation, or of maximum rate of ion-production, as a function of the sun's zenith distance χ; the unit of height is taken as H.

§ 8. THE DENSITY OF THE AIR AT THE LEVEL OF MAXIMUM ABSORPTION

It is of interest to consider the density of the air, say $\rho(\chi)$, at the level at which, $\rho(\chi)$ for any value of χ, the rate of absorption, or of dissociation (I), is a maximum. This occurs at $z(\chi) = \ln f(R, \chi)$ approximately, or $h(\chi) = h_0 + H \ln f(R, \chi)$: at this level

$$\begin{aligned}\rho(\chi) &= \rho_0 \exp\{-h(\chi)/H\} = \rho_0 \exp\{-(h_0/H) - z(\chi)\}\\ &= \rho_0/\{f(R, \chi)\exp(-h_0/H)\}\\ &= \rho_0/A\rho_0 Hf(R, \chi) = 1/AHf(R, \chi) \qquad \text{......(50).}\end{aligned}$$

Up to $\chi = 75°$, this is approximately $(\cos\chi)/AH$.

Thus the density of the air at this level is inversely proportional to H, the height of the homogeneous atmosphere, and to A, the coefficient of absorption. The former depends on the temperature and composition of the air; also A depends on the composition.

---

* This may be verified also directly from table 4.

§ 9. THE SEASONAL VARIATION IN THE MAXIMUM RATE OF ABSORPTION AT NOON

The annual variation in the maximum value of I, which by (49) (putting $Z=0$) is $I_0/f(R+z,\chi)$, over a station in latitude $l\,(=\frac{1}{2}\pi-\theta)$, may be illustrated by considering the ratio of the values at the summer and winter solstices. Reference to these two seasons will be indicated by the suffixes s and w. Since I has its maximum at noon

δ_0

$$\chi_s = l-\delta_0, \quad \chi_w = l+\delta_0,$$

where $\delta_0 = 23^\circ{\cdot}5$. Now $I_0 = \beta S_\infty/H \exp 1$, and while β and S_∞ are unlikely to undergo any annual variation, it is possible that H may do so. Taking account of this, the required ratio is

$$I_s/I_w = \{H_w f(R+z,\chi_w)\}/\{H_s f(R+z,\chi_s)\} \qquad \ldots\ldots(51).$$

It may be noted that, by (50),

$$I_s/I_w = \rho_s/\rho_w \qquad \ldots\ldots(52),$$

where ρ_s and ρ_w are the densities $\rho(\chi)$ at the levels of maximum I at the two seasons.

For $\chi \leqslant 75^\circ$, and therefore up to the latitude $75^\circ - 23^\circ{\cdot}5$ or $51^\circ{\cdot}5$ (which happens to be the latitude of London), $f(R+z,\chi)$ is equal to $\sec\chi$ within 2 per cent. (taking R to be about 650). Thus, up to this latitude,

$$I_s/I_w = \{H_w \cos(l-\delta_0)\}/\{H_s \cos(l+\delta_0)\} \text{ approximately} \qquad \ldots\ldots(53).$$

The following are the values of the ratio I_sH_s/I_wH_w (which is equal to I_s/I_w, if $H_s=H_w$) for various latitudes:

Latitude	0	15	30	45	50	55	60
I_sH_s/I_wH_w	1	1·26	1·67	2·54	3·15	4·27	7·09

§ 10. THE DAILY VARIATION IN THE RATE OF ION-PRODUCTION

The daily variation in the rate of ion-production at a given level z depends on the geographical latitude (l) of the point, and the season. If $R=650$, then at times and places at which χ does not exceed 75°, the figures 1–5 of part I remain valid, because $f(650,\chi)$ is practically equal to $\sec\chi$, as assumed in part I, up to $\chi=75^\circ$.

For greater values of χ, the values of I/I_0 given in part I are in error by more than 2 per cent., if R is 650 or less. In particular, I/I_0 does not vanish when $\chi=90^\circ$, but is still appreciable for even greater values of χ, corresponding to points at places where at ground level the sun is below the horizon; $\chi=90^\circ$ corresponds to ground sunrise or sunset.

The following method may be adopted to illustrate how I/I_0 depends on height and on χ when the sun is near (above or below) the horizon.

The equation (9) may readily be transformed to

G

$$f(R+z,\chi) = e^z\{1-z-\ln(I/I_0)\} \equiv G(z, I/I_0) \qquad \ldots\ldots(54),$$

or, the small difference between $f(R+z,\chi)$ and $f(R,\chi)$ being neglected,

$$f(R,\chi) = G(z, I/I_0) \qquad \ldots\ldots(55),$$

in which χ is involved only on the left, and z only on the right.

The graph of $G(z, I/I_0)$ as a function of z is readily plotted for any assigned value of I/I_0; G is positive from $z = -\infty$ to $z = z_0 \equiv 1 - \ln(I/I_0)$, which is positive, and beyond this value G is negative. As $z \to -\infty$, $G \to 0$ by positive values, while as $z \to \infty$, $G \to -\infty$; G has one maximum value, equal to I_0/I, for $z = z_m \equiv -\ln(I/I_0)$. Thus for any value of $G < I_0/I$, there are two corresponding values of z; moreover there is one value of χ such that $f(R, \chi)$ is equal to this value of G. The two values of z will be said to correspond to these values of χ and I/I_0; they indicate the heights at which I/I_0 has the assigned values, over any place from which the sun's zenith distance is χ. For any value of I/I_0, there is one value of χ, say χ_m, for which the two corresponding values of z coalesce; this is the χ corre-

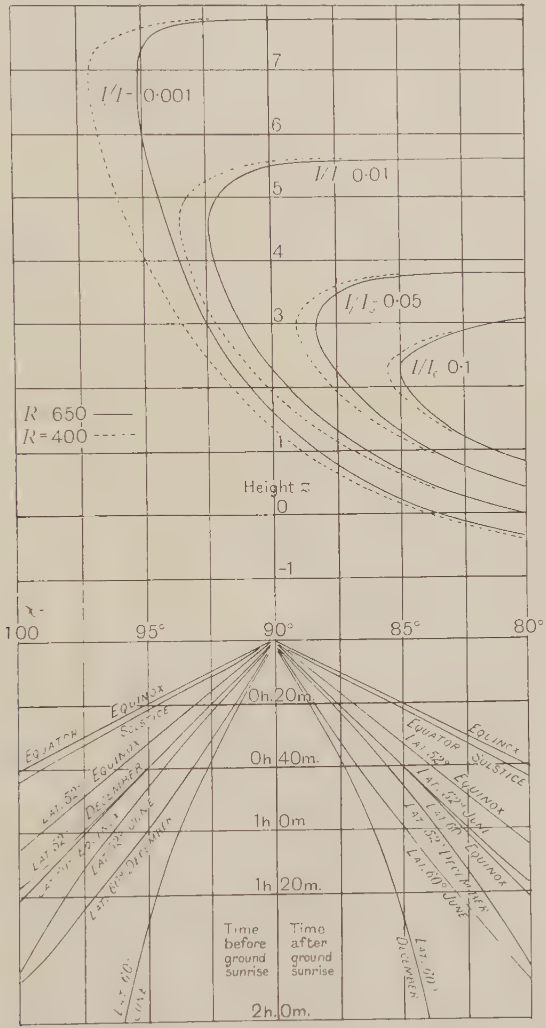


Fig. 20.

sponding to the maximum value, I_0/I, of G, and the value of z is z_m or $-\ln(I/I_0)$. All the other values of χ corresponding to I/I_0 are less than χ_m.

Figure 20 shows the heights and times for which I/I_0 has the values 0·001, 0·01, 0·05, and 0·1, for values of χ near 90°. The graphs are drawn for two values of R, viz. $R = 650$ and $R = 400$. The lower part of the diagram indicates the relation between χ and time—now measured from the epoch of ground sunrise ($\chi = 90°$)—for various latitudes and seasons; the lower left-hand curves refer to the period before sunrise, and the right-hand curves to the period after sunrise.

It appears that if $R = 650$, I/I_0 first attains the value 0·01 at a height $z = 4·6$ approximately, at the time when $\chi = 92°·4$; at the equator this time is about 10 minutes before ground sunrise, while in latitude 52° the corresponding time before sunrise varies from 16 minutes at the equinox to 20 in December and to 22 in June; the interval increases somewhat rapidly with increasing latitude. The value $I/I_0 = 0·001$ is first attained at a height $z = 7$ approximately, at about 20 minutes before ground sunrise at the equator, or 40 minutes in latitude 52° in December. The figure well illustrates the rapid downward penetration of the radiation during the period of dawn.

§ 11. THE DISTRIBUTION AND VARIATIONS OF ION-DENSITY

The corrections here made in the value of I/I_0, allowing for the earth's curvature, modify the distribution and variations of ion-*density* found in part I, but so long as the same physical assumptions are adopted, the method of calculation is the same as indicated in §§ 9–11 of part I.

Since, for any assigned values of χ and z, the true value of I here calculated exceeds the value used in part I (except when $\chi = 0$, i.e. at noon at the point immediately beneath the sun, when the two are equal), the corresponding value of ν, or n/n_0, will be greater, at all times throughout the day and night, than was formerly deduced. The excess ion-production is due to the slightly greater absorbing area presented by the earth's atmosphere than was considered in part I; it is readily seen that the excess is proportionately least at the equator, and increases with latitude.

The changes in the values of n/n_0 formerly calculated, consequent on taking correct account of the earth's curvature, are best illustrated by graphs showing a few particular cases. This has been done for the equator and for latitude 60°, at the equinox (figures 21, 22), and for latitude 60° also in midsummer and midwinter (figures 23, 24); the parameter σ_0 has been taken as 1·25 throughout. The corrected curves are the full lines, and the original curves are shown by dotted lines, for comparison. The epoch of ground sunrise ($\chi = 0$) is indicated in each case; in the two equinoctial figures (21, 22) it is 6 a.m. It is found that the change in the pre-dawn value of n/n_0 is too small to be shown on the diagrams.

At the equator at the equinoxes the initial rise of n/n_0 occurs about 10 minutes earlier than was inferred in part I. From one hour after ground sunrise, the corrections to the old results are small, and the curves are not reproduced for the period after $7^h\ 30^m$. The equatorial curves at the solstices would differ only very slightly from those shown for the equinox in figure 20.

In latitude 60° at the equinoxes the initial rise of n/n_0 becomes appreciable at 20 or even 30 minutes before ground sunrise (figure 22); at ground sunrise n/n_0 is already 0·05 at $z = 4$. From about 8 a.m. the original and corrected curves are nearly identical.

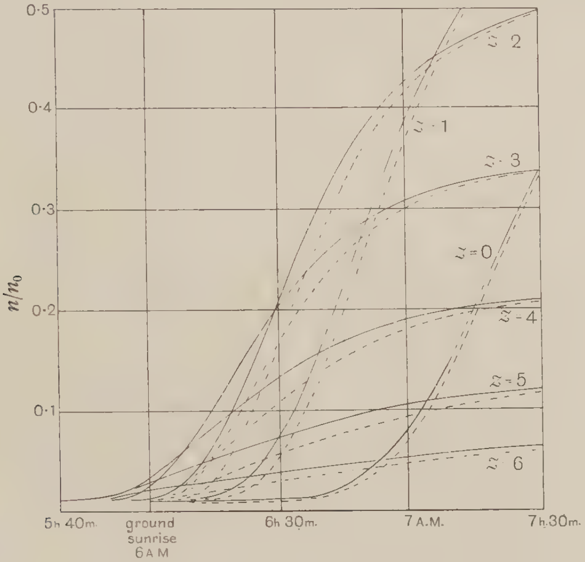


Fig. 21. Equator, equinox, $\sigma_0 = 1/25$.

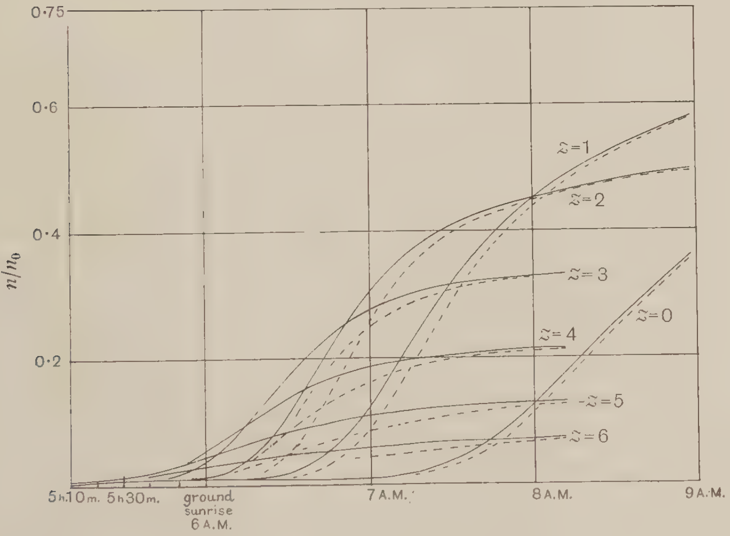


Fig. 22. Latitude 60°, equinox, $\sigma_0 = 1/25$.

In latitude 60° at midsummer (figure 23) the dawn rise of n/n_0 begins at about

1 hour before ground sunrise; at ground sunrise n/n_0 is almost 0·1 at the level $z = 4$. From 6 a.m. onwards the corrections to the original curves become small.

In the same latitude at midwinter (figure 24) the initial rise of n/n_0 begins at about 50 minutes before ground sunrise; at ground sunrise n/n_0 is about 0·07. At this season the corrections to the original curves are of importance throughout the period of daylight, though becoming small towards sunset; at noon they are quite con-

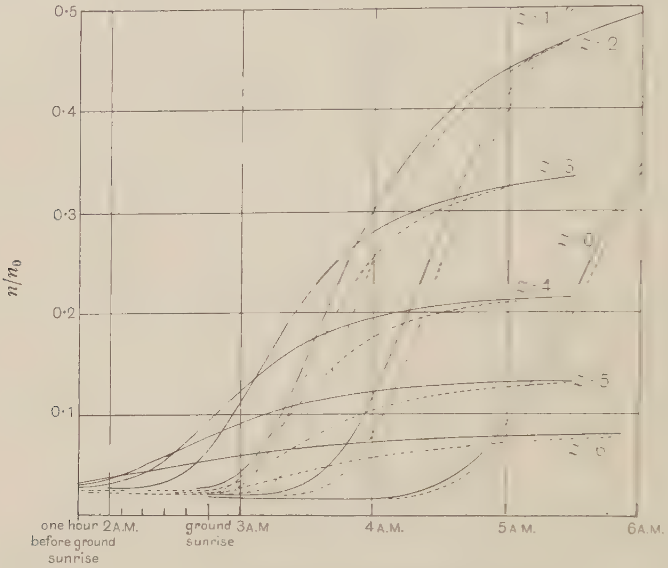


Fig. 23. Latitude 60°, summer, $\sigma_0 = 1/25$.

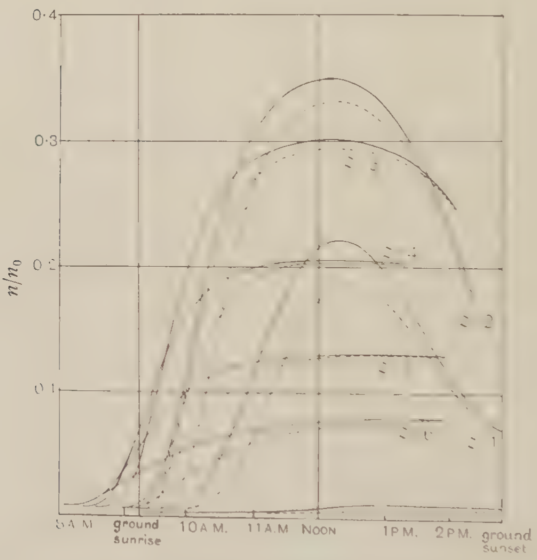


Fig. 24. Latitude 60°, winter, $\sigma_0 = 1/25$.

siderable. This is because χ is large throughout the day, and so there is a material difference between $\sec\chi$ and $f(R, \chi)$ over this period, instead of only near dawn as in the other cases.

For the latitude of London (51°·5) the interval before ground sunrise at which n/n_0 begins to increase will be somewhat less than that calculated here for latitude 60°. It would therefore appear to agree well with the interval (rather less than an hour) observed by Prof. E. V. Appleton* in his recent measurements of the electron density in the lower ionized layer of the upper atmosphere.

It is of interest to consider how n/n_0 or ν varies near dawn. The equation of change is

$$\sigma_0 (d\nu/d\phi) = (I/I_0) - \nu^2;$$

during the night $I/I_0 = 0$, so that $d\nu/d\phi$ is negative. In the latter part of the night ν is nearly constant, and small; its value (ν', say) depends on the season, latitude, and on σ_0. In figures 21–24 ν' is about 0·01 at the equator (and, in winter, at latitude 60°), rising to 0·025 in latitude 60° in summer (these values depend on σ_0 and are purely illustrative: probably they are smaller than the true values in the ionized layers of the atmosphere). The value of ν becomes stationary when $I/I_0 = \nu'^2$, which is less than 1/1000 in the above cases; figure 20 shows that I/I_0 first attains the value 1/1000 when $\chi = 95°$. From this time ν will increase, and at first, while ν^2 is still small, and I/I_0 several times as great as ν^2, the solution of the above equation will be approximately

$$\nu = \nu' + \sigma_0 \int_{\phi_0}^{\phi} (I/I_0)\, d\phi,$$

where ϕ_0 denotes the sun's hour angle at the instant when $I/I_0 = \nu'^2$.

§ 12. ACKNOWLEDGMENTS

In conclusion I wish to acknowledge assistance received from Miss M. C. Gray, M.A., and Miss V. F. White, M.Sc., who made most of the detailed numerical calculations involved in this paper, and to Mr W. Reeve, Miss V. Hatcher and Miss R. Rossiter, who assisted in the preparation of the diagrams. I wish also to thank the Department of Scientific and Industrial Research for a grant for payment for some of the assistance received in this work.

---

* E. V. Appleton, *Nature*, Feb. 7, 1931.

A TIME BASE FOR THE CATHODE-RAY OSCILLOGRAPHY OF IRREGULARLY RECURRING PHENOMENA

By G. I. FINCH, R. W. SUTTON and A. E. TOOKE
Imperial College of Science

Received March 28, 1931. *Read June* 5, 1931.

ABSTRACT. An account is given of a linear neon-lamp time base by means of which cathode-ray oscillograph traces due to recurring electrical or magnetic phenomena can be accurately superimposed, even though the train frequency be subject to wide and irregular variations. The underlying principle of this time base lies in the use of a glowing neon lamp which is extinguished by energy furnished either by the phenomenon under investigation or by some other phenomenon associated therewith.

§ 1. INTRODUCTION

Relatively slight coupling usually suffices in the case of either the Anson-Pearson flashing neon lamp* or the "ticking grid" (Appleton, Herd and Watson-Watt†) time base to ensure satisfactory superposition of repeated cathode-ray oscillograph traces of the relationship between time and regularly recurring, similar, electrical or magnetic phenomena such as are, for example, associated with either continuous undamped oscillations or regularly recurring trains of either damped or undamped oscillations of constant frequency and similar amplitudes. In order, however, to ensure synchronism, in the case of trains of similar phenomena where the train frequency varies, recourse must be had to tighter coupling between the circuit under examination and that of the time base, the degree of which must be increased with increasing irregularity of the train frequency, with consequent increase in the trace distortion due to such coupling. Further, the more erratic the train frequency, the poorer will be the trace synchronism, with the result that the figures become blurred and indistinct, until, finally, with even the closest permissible coupling, the individual traces can no longer be even approximately superposed.

The time base to be described below was developed with a view to the study of ignition-coil phenomena. These consist in the main of trains of either more or less damped oscillations or of non-oscillatory phenomena recurring at irregular intervals. These train-frequency irregularities are due in the main to the contact-breaker, the speed of the cam drive of which is seldom constant except over short intervals. Furthermore, the cam surfaces, of which there are usually 4, 6 or 8, are not uniform (except within the limits attainable by mass production processes of manufacture), nor are the separate cam angles equally disposed about the axis of rotation of the cam. A further contributory cause of such irregularities is that due to unavoidable play of the cam spindle in its bearings.

---

* Standard Telephones and Cables, Ltd., *Bulletin*, G 577, pp. 24 and 25.
† *Proc. R.S.* A, 111, 615 (1926).

§ 2. FLASHING HYSTERESIS IN A NEON LAMP FLASHING CIRCUIT

In order to render clear the operation of the time base to be described below, it will be necessary to discuss certain characteristic properties of a neon lamp discharge tube incorporated in a circuit such as is shown in figure 1. This is a modification of the well-known Anson-Pearson flashing circuit adapted for use as a linear, or nearly linear, time base for the purposes of cathode ray oscillography.

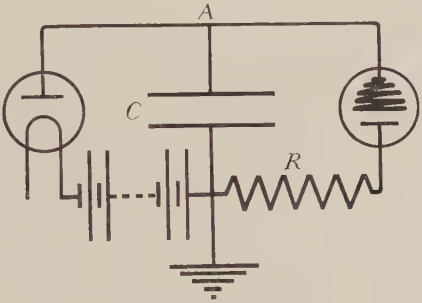


Fig. 1.

The circuit has been drawn in the conventional manner and therefore needs no further explanation, beyond pointing out that the diode must be operated under saturation conditions and that the time-scale plates of the oscillograph are connected to the point A and earth, i.e. across the condenser C.

Provided the current flowing through the diode is not excessive, C charges up to the flashing potential of the neon lamp at a linear rate and then discharges through R and the lamp until the voltage across the condenser falls to a value at which current ceases to flow through the lamp, whereupon the cycle of operations recommences, the lamp flashing once during each cycle. If, however, the current through the saturated diode be increased by brightening of the filament, a point will be reached when the lamp suddenly ceases to flash, but glows steadily. Let this critical current value be i_g. If the diode current be now lowered, flashing is not resumed until the current is reduced to a value, i_f, which may be considerably below i_g. This phenomenon may be termed "flashing hysteresis," by analogy with the "oscillation hysteresis" of an oscillating triode which has been studied by Appleton and van der Pol*. The difference, $i_g - i_f$, will serve as a measure of the flashing hysteresis.

i_g
i_f

---

* *Phil. Mag.* **43**, 177 (1922).

If the constants of the circuit shown in figure 1 could be so chosen that the hysteresis $(i_g - i_f)$ were small and that the voltage across the lamp with i_g flowing were equal, or nearly equal, to the extinction potential, then it would appear that, under such conditions, a small momentary reduction of i_g to below i_f should result in extinction of the lamp, whereupon the ensuing charge-flash cycle should terminate in a condition of steady glow due to the renewed steady flow of i_g through the lamp. Various ways at once suggest themselves in which the necessary momentary reduction of i_g could be brought about by means of a small fraction of the energy associated with a transient electrical or magnetic phenomenon of which it is desired to obtain an oscillographic record. Further, in the case where similar phenomena are repeated, exact superpositions of the resulting traces should result, independently of uniformity or otherwise in the interval times between successive phenomena.

§ 3. EXPERIMENTAL

Whether or not the circuit, figure 1, can be employed in the manner outlined above depends primarily upon the extent to which flashing hysteresis can be reduced. The following experiments were therefore carried out with the object of elucidating this matter. The circuit employed was similar to that shown in figure 1. A three-range (0–120, 0–240, 0–360 μA) microammeter was inserted in the anode circuit between the diode and A; and, instead of a single neon lamp, two de-capped beehive-pattern "osglim" lamps with ballast resistances removed, were used in series, in order to obtain a sufficient trace-amplitude with the oscillograph employed. R was a non-inductively wound variable plug-in resistance, and C a variable air-dielectric condenser. Further apparatus consisted of a von Ardenne cathode ray oscillograph and the neon lamp time base (figure 18) which forms the subject of this communication.

§ 4. DETERMINATIONS OF FLASHING HYSTERESIS

The horizontal deflection plates of the oscillograph were connected through a suitable biassing battery to A, figure 1, and earth respectively. The vertical plates were earthed. A horizontal line traced by the cathode-ray spot on the oscillograph

Table 1.

C, μF	R, w													
	90,000			50,000			30,000			20,000			10,000	
	i_f	i_g	$(i_g - i_f)$	i_f	i_g	$(i_g - i_f)$	i_f	i_g	$(i_g - i_f)$	i_f	i_g	$(i_g - i_f)$	i_f	i_g
0·0003	87	138	51	90·5	300	213	93	312	219	93	360	267	93	360
0·00055	87	96	9	90·5	252	161·5	93	255	162	96	366	270	96	390
0·001	90	96	6	96	105	9	100·5	114	13·5	99	270	171	100	360
0·0025	91·5	97·5	6	96	105	9	100·5	114	13·5	97	150	52·5	100·5	270
0·005	93	97·5	4·5	97·5	103	5·5	102	111	9	103·5	132	28·5	103·5	171

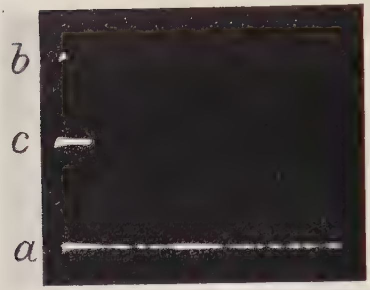


Fig. 2.

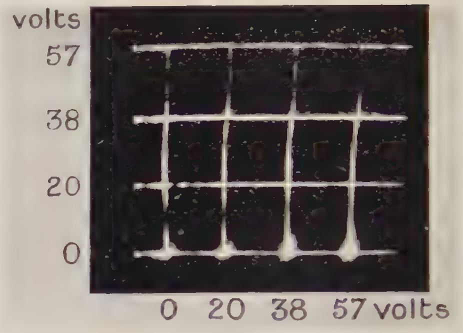


Fig. 3.

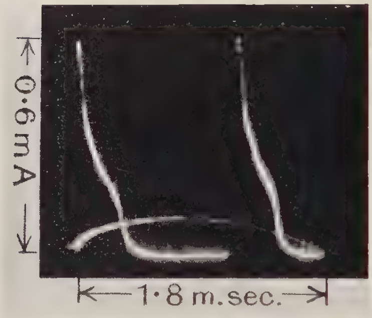


Fig. 4.

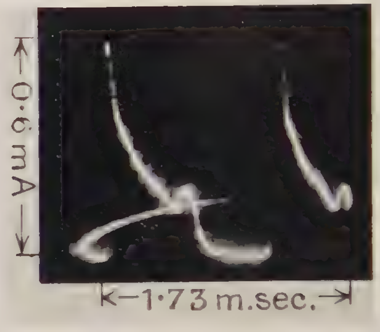


Fig. 5.

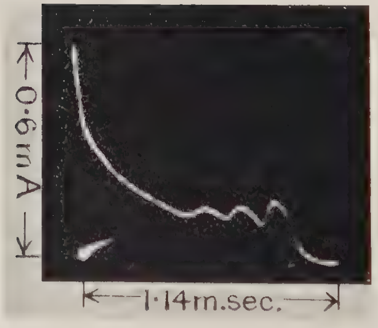


Fig. 6.

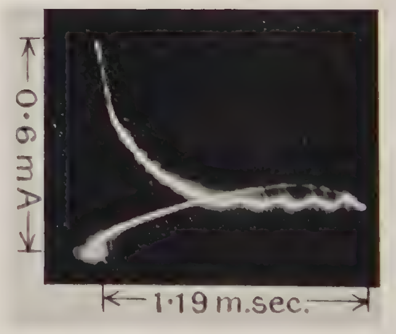


Fig. 7.

screen indicated that the neon lamps were flashing (figure 2 *a*). On increase of the diode current a point was reached when the line trace collapsed into a stationary cathode ray spot, showing that flashing had ceased (figure 2 *b*). The corresponding current i_g was read off on the microammeter. The diode current was now reduced until the spot gave way to the line trace (figure 2 *a*) on resumption of flashing conditions, the corresponding diode current being i_f. In table 1 values of i_f and i_g obtained in this manner are given in microamperes. They show the relationship between the value of C, R and flashing hysteresis for two neon lamps in series. It will be seen that low hysteresis is favoured by an increase in either C or R, and that these have critical values at which an abrupt change occurs in the magnitude of the hysteresis.

Below the heavy stepped line in the table lies a well-defined region of comparatively low hysteresis.

§ 5. FLASHING CHARACTERISTICS OF THE CIRCUIT OF FIGURE 1 UNDER LOW HYSTERESIS CONDITIONS

At first sight the results incorporated in table 1 did not appear encouraging, because the extent of the hysteresis, even under the most favourable conditions, amounted to a considerable fraction of either i_f or i_g. It was clear, however, that $(i_g - i_f)$, as determined in the manner outlined above, was virtually a measure of static hysteresis; and the fact that flashing, when once established, persisted until i_f had been increased to i_g suggested that a suitable momentary impulsive lowering of i_g to a value intermediate between i_g and i_f might suffice to extinguish a lamp glowing steadily with the current i_g. It was, indeed, occasionally observed that, with circuit conditions favourable to low hysteresis, when the diode current was gradually increased from the value i_f, the line trace on the oscillograph screen first collapsed to a much shorter line trace (figure 2 *c*) which, in its turn, collapsed to a spot when the current was further increased by an amount which could hardly be read on the microammeter; and further that, when conditions were such as to produce this short line, even such slight coupling as that due to the capacity between the oscillograph plate pairs sometimes sufficed to extinguish the glow, and thus to cause the lamp to flash once each time the vertical deflection plates were suddenly charged up to a suitable potential difference, the horizontal plates being connected to A and earth, figure 1. The short line trace was clearly due to the occurrence of oscillations of small amplitude in the lamp circuit. With a view to elucidating the rôle clearly played by the small amplitude oscillations in reducing the stability of the glowing condition of the lamps when passing the current i_g, it was decided to obtain a series of oscillograms of current time relationships and of the dynamic voltage/current characteristics of lamps flashing with various values of C and R in the circuit (figure 1).

The current time traces were obtained by connecting the vertical deflection plates of the oscillograph across R, and the horizontal plates to the neon time base circuit to be described below; and the voltage current characteristic traces by connecting the vertical deflection plates across R and the horizontal plates across the lamps, suitable bias being inserted in the lead from A, figure 1, to the oscillograph in order to bring the cathode-ray spot approximately into the centre of the screen when A was at a potential above earth equal to the extinction voltage of the lamps.

Of the many oscillograms recorded photographically in this manner those reproduced here (figures 4 to 17 and 19 to 24) will suffice to bring out clearly the point at issue. The exposures employed in photographing these traces were such that each oscillogram is compounded of several thousand superimposed traces. The definition of the resulting oscillograms is therefore a criterion of the degree of synchronism between the circuit phenomena under investigation and the action of the time-base employed.

§ 6. THE CURRENT TIME OSCILLOGRAMS

Ten oscillograms, showing the relationship between the current traversing the lamps under flashing conditions with various values of R and C and diode current, are reproduced in figures 4 to 11, in which the time scale is horizontal and the current scale vertical. The experimental data relating to these oscillograms are summarized in table 2.

Table 2.

Oscillogram, figure	R (ohms)	C (μF)	Diode-current (μA)	Hysteresis, $i_g - i_f$ (μA)	Remarks
4	97,000	0·0010	90	6	Little short of glowing
5	97,000	0·0010	93		Nearer to glowing
6	97,000	0·0010	94		Still nearer to glowing
7	97,000	0·0010	95		Just below glowing
8	97,000	0·0010	96		Just glowing steadily
9 *a*	32,000	0·0010	112	13	
9 *b*	32,000	0·0010	113		
9 *c*	22,000	0·0010	113		
10	33,000	0·00055	250	160	
11	53,000	0·00055	250	161	

Figure 3 is a reproduction of the voltage deflection scale which served for measuring up the oscillogram, figure 4. All other oscillograms reproduced herein, except that of figure 9, are approximately to this scale.

The oscillograms (figures 4 to 11) show that, on striking, the discharge current through the lamps rises so rapidly to a peak value that the corresponding trace is barely visible on the photographic record. The discharge current then falls much more slowly and at a non-uniform rate and, provided the diode current is sufficiently far below i_g, finally approaches zero in an exponential manner (figure 4), whereupon the steady diode current recharges C until flashing recurs. When the diode current is slightly increased a similar sequence of events occurs with the exception that the discharge current, shortly before falling to zero, executes a single or partial oscillation (figure 5) about a mean value corresponding approximately to that of the diode

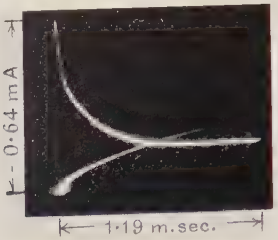


Fig. 8.

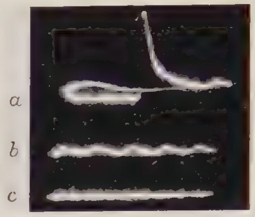


Fig. 9.

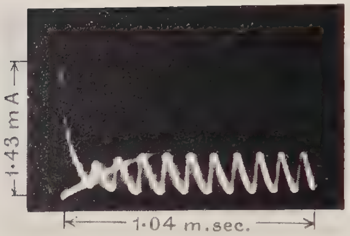


Fig. 10.

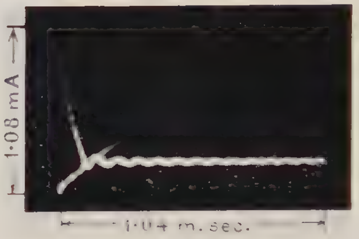


Fig. 11.

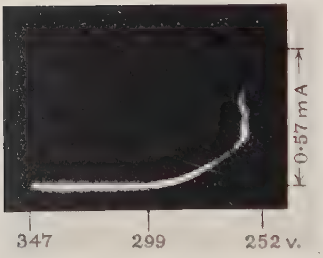


Fig. 12.

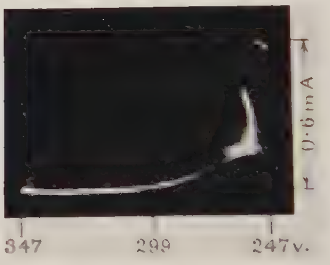


Fig. 13.

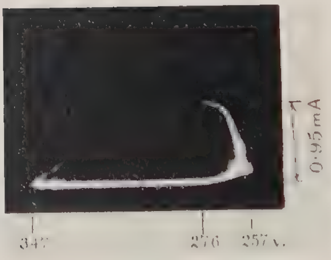


Fig. 14.

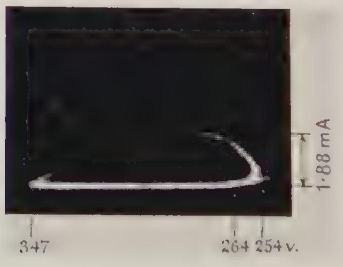


Fig. 15.

To face p. 507]

current. A further increase in the diode current results in the setting up of a train of unstable oscillations which increase in amplitude (figures 6 and 7) until, after attaining a critical amplitude value, the discharge current decays to zero (figure 6), and the lamps are extinguished. When the diode current is equal to or above i_g the discharge current falls smoothly and without executing oscillations to the diode-current value (figure 8) at which it remains constant, and the lamps in consequence glow steadily. Resistance coupling was resorted to in order to ensure synchronism in the case of the oscillograms figures 4 to 8, a variable 1-megohm resistance, in nearly every case all in, being employed for this purpose. This fact alone will serve to illustrate the ease with which is set up a train of oscillations of increasing amplitude which rapidly lead to extinction of the lamps, provided the circuit conditions are suitable.

In securing the oscillograms shown in figure 9, precautions were taken to reduce and confine the coupling between the circuit of figure 1 and that of the time base as far as possible to that due to the capacity between the oscillograph plate pairs alone. In figure 9 *a* the diode current was less than 1 per cent. below i_g. In figure 9 *b* the diode current was practically equal to i_g; the perfect superposition of the current time traces of the low-amplitude saw-toothed oscillations obtained adequately demonstrates the sensitivity of the time base circuit employed and the minute amount of coupling required to ensure synchronism. In the case of figure 9 *c* the diode current was slightly above i_g, and in order to secure a trace it was necessary to reduce the time-base diode current to below its i_f value.

The oscillograms shown in figures 10 and 11 are representative of those which could be obtained when the circuit conditions were such as to give large hysteresis values. Comparatively tight coupling had to be resorted to in order to obtain these oscillograms. According to the value of the diode current, the discharge current either (i) fell to zero, in a manner similar to that shown in figure 4 (diode current $< i_g$), or (ii) finally executed undamped saw-tooth oscillations as in figure 10 (diode current $\fallingdotseq i_g$), or (iii) gave rise to damped oscillations as in figure 11 (diode current rather higher than in (ii) but still $\fallingdotseq i_g$).

§7. THE DYNAMIC VOLTAGE/CURRENT CHARACTERISTIC OSCILLOGRAMS

The current/time records discussed above adequately demonstrate the metastability, under suitable circuit conditions, of the glowing state of the neon lamps passing a current equal to i_g, and the ease with which extinction may under those conditions be brought about. They further show that the initial portion of a time-base stroke produced by means of the circuit figure 1 cannot be linear; because the discharge current after falling below i_g does not fall to zero instantaneously, but does so in an exponential manner, during which time the diode current is divided between that flowing through the lamp and that which charges up C. The series of voltage/current oscillograms shown in figures 12 to 17, in which the current and voltage scales are vertical and horizontal respectively, afford a clear insight into the effect of the values of C and R upon the lamp voltage when the current i_g or one approximately equal thereto is passing, and into the value of extinction voltage ensuing upon reduction of i_g in the manner previously outlined. The flashing potential under static conditions for the two neon lamps in series was found to be 338 volts. The experimental data relating to the oscillograms, figures 12 to 17, are given in table 3.

These oscillograms show that in every case the lamp voltage falls, on flashing, to a value considerably below that of the extinction potential under the corresponding dynamic conditions. Further, for present purposes*, it will be sufficient to draw attention to the following facts brought out by these oscillograms: The difference between the values of the dynamic extinction and flashing potentials, i.e. the length of the linear portion of the time base stroke, increases (i) as R is decreased (figures 12, 13, 14 and 15) and (ii) as C is increased (figures 14, 16 and 17). It is clear, therefore, that, in order to obtain the greatest possible length of linear stroke with the time base, it is essential that the values of C and R should be so chosen as to be as near as possible to, but below, the heavy stepped line in table 1.

Table 3.

Oscillogram figure	R (ohms)	C (μF)	Hysteresis (μA)	Remarks
12	90,000	0·001	6	Well below glowing
13	90,000	0·001	6	Nearly glowing
14	30,000	0·001	13·5	Nearly glowing
15	10,000	0·001	258	
16	30,000	0·0035	11	Nearly glowing
17	30,000	0·00055	162	

§ 8. DESCRIPTION OF THE TIME BASE

The practical circuit of the time base which has been developed on a basis of the considerations outlined above is shown in figure 18. The arrangement of filament rheostats shown therein permits of a fine control of the temperature of the tungsten filament of the R-type triode, of which grid and anode are inter-connected. The microammeter, μA, can be calibrated in terms of the duration of one time stroke for known values of C, a variable 0·0003 μF condenser, which is provided with terminals to which fixed condensers of suitable capacity can be connected. The resistance R is carried in a clip-in holder, thus permitting of easy interchange of different values of R. In the interests of linearity, the unearthed side of C is connected to the corresponding time deflection plate of the oscillograph through a bias battery, instead of the usual arrangement of a condenser and leak.

Suitable coupling between the time base and the circuit under investigation can be effected in various ways. For instance, the plate P of the oscillograph can be

---

* It is our intention to discuss these and other dynamic characteristics of discharge tubes in greater detail in a further communication to the Society.

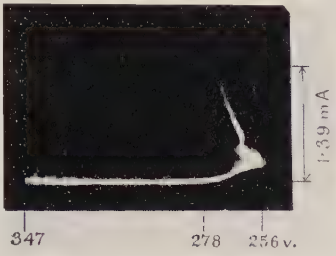


Fig. 16

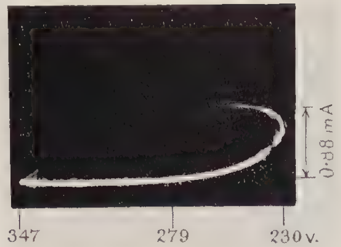
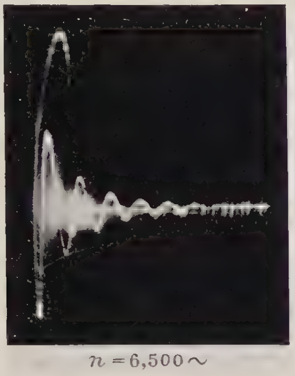
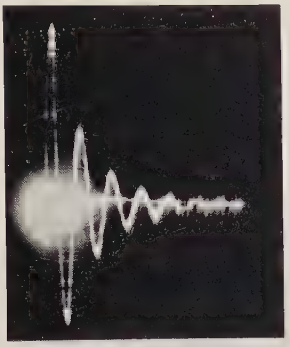


Fig. 17.



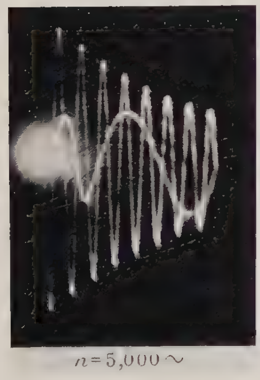
$n = 6{,}500 \sim$

Fig. 19.



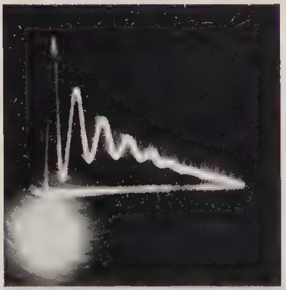
$n = 6{,}500 \sim$

Fig. 20.



$n = 5{,}000 \sim$

Fig. 21.



$n = 17{,}700 \sim$

Fig. 22.

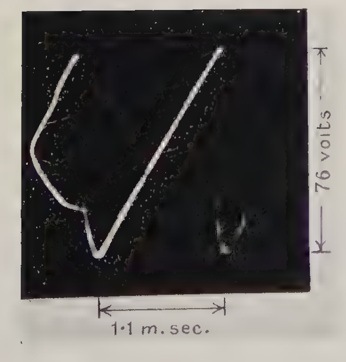


Fig. 23.

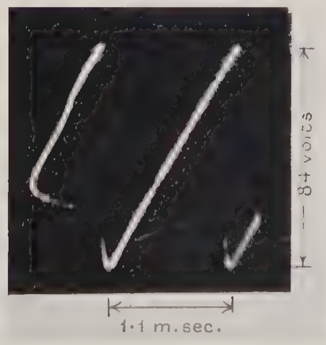


Fig. 24.

[*To face p.* 508

connected to the terminal *B*, the degree of coupling being controlled by means of the 1-megohm variable resistance shown in the diagram. Or, again, an inductance coil connected across *A* and *B* can be inductively coupled with the circuit under investigation. In certain cases we have found it of advantage to incorporate a triode adjusted to operate on bottom-bend conditions in the coupling circuit, in order to reduce interference with the phenomenon under investigation to a minimum.

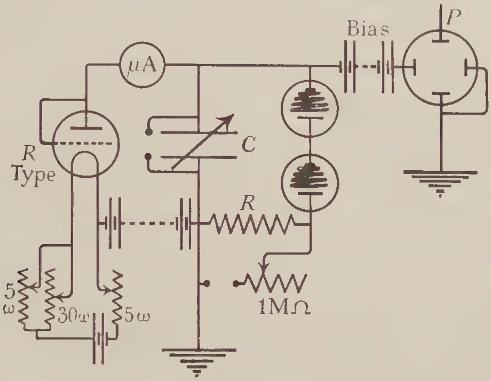


Fig. 18.

The following precautions should be taken in using the base. The high and low-tension accumulators should be first fully charged and then slowly discharged to the extent of approximately one-fifth of their capacity before use. They should be re-charged when a further two-fifths of their charge has been used up. The triode and the filament rheostats should be shielded from draughts. It is, further, essential that the insulation be good, particularly across the diode, the condenser *C*, and the neon lamps, and in order to ensure this being the case the pinches of both the de-capped diode and lamps should be well dried and varnished with shellac.

When the time base is to be operated the filament rheostats are adjusted until the diode current equals i_g. The voltage changes due to the phenomenon to be investigated are then applied to the plate *P*, and finally the coupling is adjusted until the neon lamps commence to flash in synchronism with the phenomenon. The filament and coupling adjustments will be found to be critical. Incorrect direction of coupling will result in distortion, as in figure 19, which shows the oscillations in a circuit comprising an iron-cored inductance of 3 mH and a capacity of 0·2 μF. In this case not only was the direction incorrect, but the amount of coupling was excessive also. Similar oscillograms, but obtained with correctly adjusted coupling, are shown in figures 20 (iron-cored 3 mH – 0·2 μF) and 21 (air-cored 5 mH – 0·2 μF). It will be seen that, in the cases of the two latter oscillograms, non-linearity of the time base is confined to the initial portion of the first half-oscillation. Figure 22 shows the current oscillations in a 3000 ohms resistance shunting the secondary of an induction coil. It may be mentioned that in photographing these last four traces the camera lens was stopped down as far as possible (*f* : 42), and that during exposure (about 30 sec.) the speed of the 8-cam contact breaker employed was made to vary in an erratic manner between about 100 and 800 r.p.m. A train frequency higher than 6400 per minute was not employed with the iron-cored inductance circuits because the circuit arrangements were such that, at higher speeds, the value of current flowing in the inductance at break would have varied inversely with the time of make by the contact-breaker. The definition of the oscillograms obtained is ample testimony to the degree of accuracy with which the cathode-ray traces have been superimposed.

Finally, the oscillograms reproduced in figures 23 and 24 in which the relationship between the potential across *C* and time is shown, demonstrate the uniformity in the rate of charging up of *C*, and hence the linearity of the time base, in all but a short initial stage. They confirm, further, the conclusion that the nearer the values of *C* and *R* lie to the heavy stepped line in table 1 in the region below that line, the greater is that proportion of the time-base stroke which is drawn at a linear rate. The rate of rise of voltage shown in figure 24 is, indeed, uniform practically throughout.

§ 9.

We wish to place on record our appreciation of the assistance afforded to us by Messrs Ferranti Ltd., who generously placed at our disposal such apparatus as was required in the prosecution of this investigation.

NOTES ON THE OSCILLOGRAMS, FIGURES 4 TO 11.

Flashing occurs simultaneously in the neon lamp of the time base and circuit under investigation at the origin of the coordinates, except in the case of figure 9 *a*.

Figures 4, 5 *and* 6: Time-base-diode current = i_g; the time base is "tripped," i.e. the time base lamps extinguished by flashing of the lamps in the circuit under investigation.

Figures 7, 8, 10 *and* 11: Time-base-diode current = i_g; time base "tripped" by flashing of circuit under investigation, which is, in its turn, "tripped" by flashing of time base.

Figures 9 *a*, *b*: Time-base-diode current = i_g. Time base "tripped" by low amplitude saw-toothed oscillation of circuit under investigation. In figure 9 *a* the first saw-toothed oscillation is followed (after flashing of time base) by a second one of increased amplitude which leads to extinction. In the case of figure 9 *b*, conditions are such that flashing of the time base does not increase the amplitude of the saw-toothed oscillations to an extent sufficient to bring about extinction of the lamps in the circuit under investigation.

NOTE ON THE OSCILLOGRAMS, FIGURES 12 TO 17.

Flashing occurs at 347 volts. The discharge current then rises and the voltage across the lamps falls with such rapidity that the corresponding trace is barely visible. The voltage invariably falls below the extinction potential, i.e. that voltage at which current ceases to flow (299 volts in the case of figure 12).

NOTE ON THE OSCILLOGRAMS, FIGURES 21 AND 22

The beginning of the first half-cycle trips the time base and the oscillogram is described. When the time-base lamps flash, the cathode-ray spot returns at an exponential rate to zero, the initial rate of such return being far more rapid than that of the true time stroke in the forward direction; hence, in figure 21, the expansion of oscillations which occurs on the return stroke; and in figure 22 the slope of the return stroke is seen to be much less than that of the mean line about which the current oscillates. In both cases, the spot remains at zero until the beginning of the first half-oscillation of another train trips the time base afresh.

DISCUSSION

Prof. A. O. RANKINE remarked that the traces shown in the illustrations showed very little blurring. The phenomena represented must therefore have been very similar at each recurrence.

Mr O. S. PUCKLE. I would like to ask the authors where the connexions between the tube and the wave source are made. I presume that the source is connected to the two horizontal plates of the oscillograph, that is to say to the right-hand side of the resistance R, figure 1, so that the potential across it is used to trigger the time base. In addition I would like to enquire whether it is necessary to adjust the diode current when large changes are being made in the value of the frequency under examination, say from 1000 to 1,000,000 ~.

AUTHORS' reply. The time-base-circuit condenser is connected to one pair of plates, one of which is earthed; the source leads go to the other pair of plates, one of which is earthed while the other is connected to the neon lamp through a variable 1-$M\Omega$ resistance. Energy thus tapped off through the unearthed source-lead trips the neon lamp. It is not necessary to adjust the diode current, but the coupling between the time-base-circuit and the source may require adjustment.

THE HILGER X-RAY CRYSTALLOGRAPH AND THE CUBIC-CRYSTAL ANALYSER

By S. ZEIDENFELD, B.Sc., A.R.C.S., A.Inst.P.

Adam Hilger Ltd. Research Laboratories, London

Received June 6, 1931.

ABSTRACT. A description is given of an X-ray crystallograph designed on the principle used by Seeman(1) and Bohlin(2) in which the slit, specimen to be analysed and photographic film are disposed along the circumference of a circular camera. Typical crystallograms obtainable are shown.

The cubic-crystal analyser is described and some examples demonstrating its use are given.

§ 1. INTRODUCTION

The basic principle underlying all powder methods of X-ray crystal analysis is essentially that of Bragg(3), but owing to the impracticability of obtaining single crystals of appreciable size, his original method has been modified so as to be adaptable to the various obtainable forms of the material under investigation. This has led to such methods as those used by Debye and Scherrer(4), Hull(5), Weiss(6) and others, which, although differing slightly in their experimental arrangements, owe their success in operation to identical factors. In order to arrive at a correct determination of the atomic structure of any substance by any of the powder methods, it is essential that the substance should consist of a conglomeration of small crystals offering all possible orientations to the incident monochromatic X-ray beam. This condition is ensured by powdering the substance (filings being used in the case of metals and alloys), and spreading them into flat layers or placing them in thin celluloid containers. Rotation or oscillation will further ensure the random orientation necessary, and we would then have all the
θ possible planes present at the required orientation θ to the incident beam so that reflection should result according to the Bragg relationship

$$n\lambda = 2d \sin \theta \qquad \text{......(1)},$$

d d being the spacing between geometrically like planes,

λ λ the wave-length of the X-rays used, and

n n the order of reflection obtained.

Let us now consider the effect of a narrow circular beam of X-rays when incident upon a rod of powdered specimen situated at the centre of a circular camera (Debye and Scherrer method). Wherever it encounters a crystal plane of spacing d at a glancing angle θ such that the Bragg equation is satisfied, then the ray will be reflected, the total deviation from its original path being 2θ. But owing to the haphazard distribution of the crystals, all orientations of the reflecting plane in question will be possible, and hence the reflected ray will not lie in one single plane but will form a cone of semi-vertical angle 2θ about its incident direction as axis. The intersections of these conical surfaces with the film, which is placed round the circumference of the camera, produce a series of curved lines symmetrically placed about the point of incidence of the direct beam. Measurement of the distances between these lines leads to the evaluation of the glancing angle θ and hence to the solution of the Bragg equation.

For precise measurements it is necessary to take certain precautions and make various vital corrections. Some of the principal ones are enumerated below.

(i) Since the breadth of the spectrum lines recorded is approximately equal to the breadth of the crystalline rod, inaccuracies often occur in the measurement of the inter-lineal distances owing to the difficulty of exactly determining the centre of lines not having sharp edges.

(ii) Approximate measurements only can be made of the crystal-to-film distance. This can be partially remedied by an exposure of some standard substance, such as sodium chloride, placed in a cylindrical container of dimensions identical with those used for the substance under analysis. A high order of accuracy cannot be obtained owing to the variation of the absorption properties of the substances used.

(iii) An important error is that due to absorption, which has the effect of making the calculated value of θ greater than it should be. Corrections have been suggested from theoretical considerations by O. Pauli(7) and by A. J. Bijl and N. H. Kolkmeyer(8). Practical methods employing comparison of photographs with those of standard substances have been used by W. P. Davey(9) and R. W. G. Wyckoff(10). If the powder used is pressed into the form of a flat layer, or if flat plates are used in the analysis of metals or alloys as in Weiss's method, the discrepancies due to absorption are modified, but further sources of error are entailed by the new experimental arrangement.

(iv) In Hull's method, where flat sheets of the powder are used either in a compressed condition or between plane glass plates, and are placed normally to the X-ray beam, the errors due to absorption are negligible. However, for accurate measurements precautions must be taken to ensure that the thickness of the sheet is constant and that the surfaces are perfectly plane.

(v) In Weiss's method a plate of the metal or alloy is oscillated in the X-ray beam through any convenient angle. Errors will occur if the surface is not coincident with axis of the cylindrical camera. Corrections as suggested by A. Müller(11) must be applied.

(vi) In the above-mentioned powder methods it is necessary, in order to obtain satisfactory photographs, that the size of the crystal grains be small, that is, about 0·1 mm. to 0·005 mm. If the crystals used are too large, the spectrum lines recorded will appear broken and disjointed, which further hinders the accurate location of the mid point during measurement of the inter-lineal distances.

(vii) Finally a great practical drawback in all of the above methods is the prolonged exposure necessary, unless a powerful and therefore more expensive plant is used.

We thus see that in order to arrive at precise determinations of crystal structures the observer must take special precautions in the preparation of his specimens and in the setting up of his instrument. He must then apply corrections to his calculated results. The following paragraphs, however, describe a method of taking powder photographs without the encumbrance of the aforementioned sources of error.

§ 2. PRINCIPLE OF METHOD

Figure 1 represents diagrammatically the camera of the crystallograph. A monochromatic X-ray beam passes through the slit S and is incident upon the scattering substance placed along BC. Consider a ray striking the powder at the point B. This will be reflected from a lattice plane of spacing d and will record a spectrum line on the photographic film at the point P. The amount of deflection from its incident path, suffered by the ray, is equal to 2θ according to the Bragg equation (1), that is

$$\angle EBP = 2\theta.$$

From the geometry of the figure

$$\angle SBP = \angle SCP,$$

whence $$\angle FCP = 2\theta.$$

Thus if a ray is incident at C upon a lattice plane of the same spacing d as at B, it will be reflected to the point P. Similarly for all points along BC. Hence all the rays which strike lattice planes of identical spacings will be deflected and *focussed* upon the same point P, where a sharp image of the slit should be expected.

Again, from the geometry of the figure

$$\angle SOP = 4\theta.$$

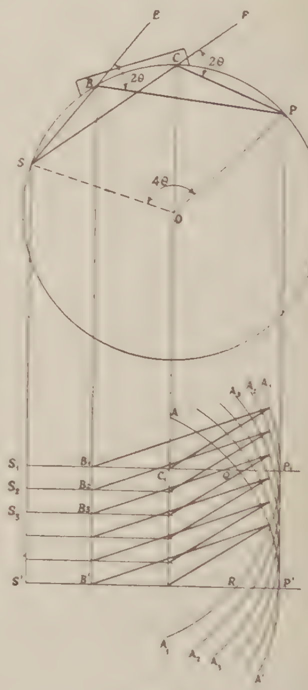


Fig. 1.

p Hence if p is the distance of spectrum line from
r slit (arc SP) and r the radius of the camera then

$$p = 4r\theta \qquad \text{......(2)},$$

whence the glancing angle can be calculated. This value of θ substituted in the Bragg equation (1) will then give the spacing of the reflecting lattice plane.

§ 3. FORMATION OF THE SPECTRUM LINES

The actual formation of the spectrum lines can be seen from the vertical projection⁽²⁾ as shown in the lower half of figure 1. Rays passing through the slit S_1S' are incident on the scattering substance at $B_1B_2 \ldots B'$, and will all be deflected at an angle 2θ. (We are considering only lattice planes of spacing d.) The deflected ray will in each case, as in the Debye and Scherrer method, describe a cone of semi-vertical angle 2θ about its incident direction, and will eventually intersect the film, forming curves $A_1A_2 \ldots A'$. The superimposition of these curves gives rise to the photographic image of shape $P_1P'RQ$, but with a sharply defined edge P_1P' which corresponds to the common tangent of the curves and is geometrically defined by equation (2). This image formation is very well illustrated in figure 2 which is an untouched reproduction of an enlargement (× 5 approximately) of a spectrum line that was actually recorded on the crystallograph. The scattering substance in this case was a sheet of annealed metallic aluminium having its crystal grains larger than would be practicable with other powder methods. Even in this case the edge is broken, but its definition is sharp enough for accurate measurement.

This edge does not always lie on the same side. As the glancing angle increases the breadth of the line decreases, as can be seen from the construction of figure 1, till a point is reached where $\theta = 45^\circ$, that is, where the semi-vertical angle 2θ of the intersecting cone $= 90^\circ$. At this position the spectral line formed is a straight-line image of the slit. If the glancing angle is still further increased the breadth of the line will also be increased, but now the sharp edge will be on the opposite side. The turning-point is given by substitution in equations (1) and (2)

$$n\lambda = 2d_0 \sin 45^\circ, \qquad\qquad d_0$$

that is
$$d_0/n = \lambda/\sqrt{2} \qquad \ldots\ldots(3\,a),$$

and also
$$p_0 = \pi r \qquad \ldots\ldots(3\,b).$$

§ 4. COMPARISON WITH OTHER POWDER METHODS

In order to facilitate direct comparison with other powder methods, the various factors affecting the accuracy of measurement will be dealt with in approximately the same numerical order as before.

(i) The breadth of line does not affect the accuracy of measurement since readings are taken on one edge only. The breadth is, however, kept within certain limits so as to prevent diffusion of the edge. This is effected by using narrower slits and a narrower width B_1B' of the scattering material (cf. figure 1).

(ii) No crystal-to-film distance need be measured. The only dimension required is that of the radius of the instrument. This is permanently fixed and can be checked by taking an exposure of some standard substance of known lattice spacings, such as sodium chloride.

(iii) Results are unaffected by absorption, that is, by the varying depth of penetration of the X-ray beam. This is shown in figure 3 where the dotted lines represent the path of the reflected rays from the interior of the scattering medium. The geometric position of the sharp edge *P* is not influenced by the amount of penetration. This is demonstrated rather well in figure 2, where the images reflected from two layers of crystals can be clearly seen at *P* and *P′*.

(iv) Care must be taken to ensure that the whole surface of the reflecting material lies on the circumference of the camera. In the case of metallic sheets this condition is easily fulfilled by bending the metal into an arc of the required radius. Powders, however, may be either compressed into the requisite shape or painted on a specially provided powder holder. The latter is a glass plate which has its face ground to a concave cylindrical curve of radius equal to the focussing radius of the camera.

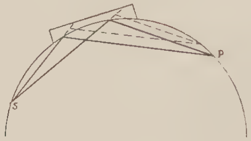


Fig. 3.

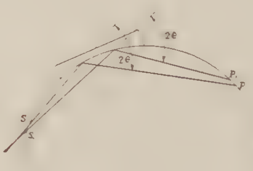


Fig. 4.

(v) There is no need to provide for the oscillation or rotation of the specimen, as the whole surface lies in the beam of the incident X-rays.

(vi) The range of crystal-grain size is shifted to a higher limit.

(vii) The exposures are greatly reduced. For example the powder photograph of copper filings was taken in 45 seconds with monochromatic CuK_α radiation generated by a Shearer tube working at peak voltage of 70,000 volts and a slit width of 0·07 mm.

(viii) A very necessary precaution is to ensure that the slit edge *S*, figure 4, is permanently fixed coincident with the circumference of the camera. The size of slit-width will then not affect the accuracy of readings since the sharp edge corresponds only to the position of *S* (cf. figure 4).

§ 5. GENERAL CONSTRUCTION OF THE CRYSTALLOGRAPH

A diagrammatic reproduction of the general assembly of the crystallograph camera is shown in figure 5. In figure 6 it is shown in the dismantled condition.

The camera itself is constructed in the form of a shallow cylinder 1 which is 4·4 cm. in height and 4·5 cm. in radius. A portion is cut away to form an angular recess for accommodating the anticathode end of a Hilger-Shearer X-ray tube. The relative position of the tube is fixed by four locating studs 4, 6, 9, 11, one of which *a*, 4 is adjustable. Once the correct position of the tube is found, its location is permanently secured by seeing that the anticathode end is making proper contact with all four studs. A great advantage which arises in having the crystallograph designed expressly for use with the Shearer X-ray tube is that we thus obtain a

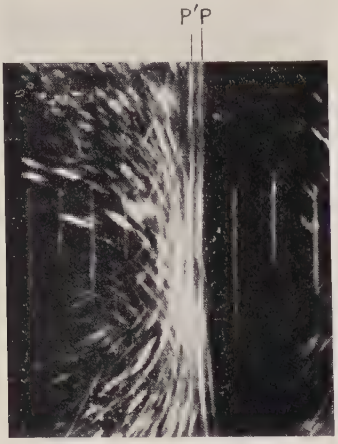


Fig. 2.

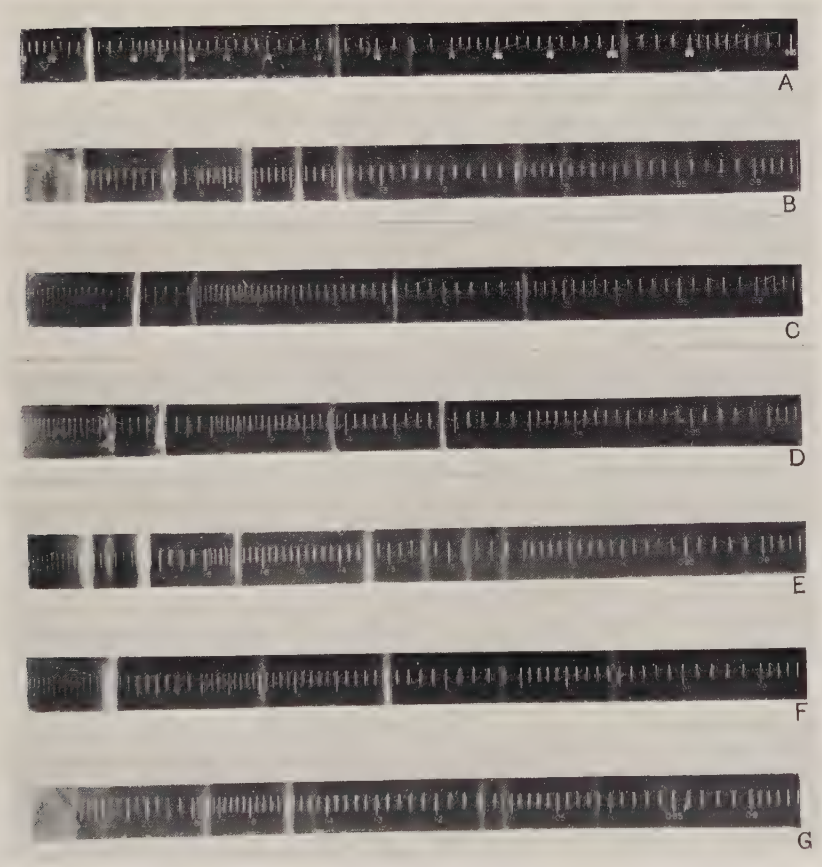


Fig. 7. Typical crystallograms. *A*, powdered sodium chloride, exposure 20 min.; *B*, powdered zinc oxide, exposure 10 min.; *C*, copper filings, exposure 5 min.; *D*, aluminium sheet (annealed), exposure 5 min.; *E*, zinc sheet, exposure 5 min.; *F*, tungsten filings, exposure 10 min.; *G*, lead filings, exposure 30 min.

maximum intensity of the incident X-ray beam, since the anticathode of the tube is directly behind its window which is itself almost in contact with the slits, figure 5.

The slit system consists of two brass jaws 5, 8 tipped with a bismuth-lead alloy and cut obliquely at angle of 30° to form knife-edges. The slit jaw S is permanently fixed, whilst slit jaw S_1 is adjustable by hand. A set of slit gauges is used for setting to the required aperture and the slit jaw S_1 is secured in position by two screws. A lead stop b prevents fogging of the film by direct or scattered radiation from the slit system. The glass specimen holder C, 13, 14, previously described, fits into the side of the camera and is secured by a light-tight cover d, 15 and two screws e, 7, 10.

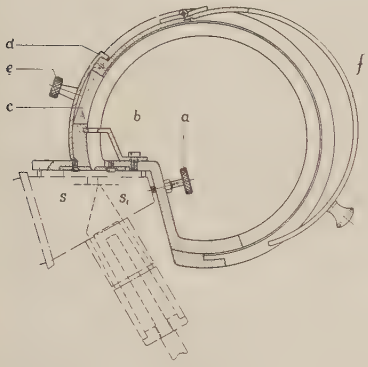


Fig. 5.

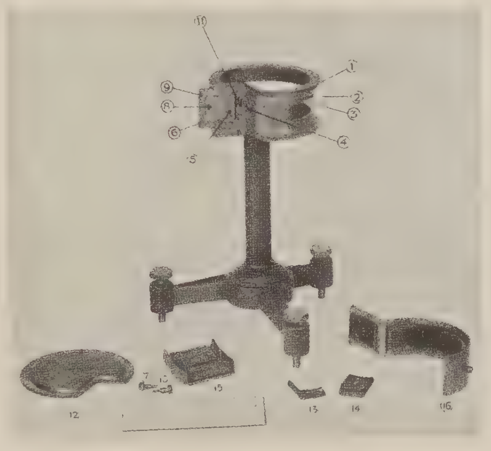


Fig. 6. Hilger crystallograph.

The photographic film is 17 cm. long and 2·5 cm. wide; it has one end punched with two accurately gauged holes and is then fitted on the two small pegs which locate it in the camera. It is then wrapped around the circumference of the camera and rests on the cylindrical surfaces 2 on either side of a wide annular slot 3 through which it is exposed to the reflected rays from the scattering medium on the powder-holder. A light-tight brass cover f, 16 clips the film into position and holds it firmly in place.

The camera is provided with a light-tight brass cover plate 12 and is mounted on a firm tripod stand provided with levelling screws, at such a height that the window of the Shearer tube is level with slit of the crystallograph.

§ 6. THE INTERPLANAR SCALE

Since the constants of the instrument are permanently fixed, it has been possible to devise a method of superimposing an interplanar scale upon the crystallogram. We get by substitution for θ from equation (2) in equation (1)

$$d/n = \lambda/\{2 \sin (\rho/4r)\},$$

that is

$$d_{hkl}/n = \lambda/\{2 \sin (\rho/4r)\} \qquad \ldots\ldots(4),$$

where d_{hkl} is the spacing between like planes whose Miller indices(12) are h, k, l.

d_{hkl}

The scale was calculated from the above relationship between d_{hkl}/n and p and gives value of d_{hkl}/n at every point of the film. It was assumed that filtered Cu-radiation ($\lambda = 1{\cdot}54$ Å.U.) had been used. This condition is obtained in practice by using a Shearer X-ray tube fitted with a copper anticathode and a nickel-foil window. The interplanar scale is contained in a separate printing-frame provided with two film-locating pins so placed as to correspond approximately to a similar pair fixed in the camera. After exposure in the crystallograph the film is removed in a dark-room and placed in the printing-frame. The interplanar scale is then printed on to the negative by exposure to white light for a fraction of a second, and development brings it up together with the crystallogram.

A screw adjustment is provided for the exact setting of the scale. This can be done by using any standard substance of known spacings and then setting the scale readings, by the method of trial and error, to coincide with the theoretical values of d_{hkl}/n of the lines obtained on the crystallogram. Sodium chloride is most frequently used as the standard and the lines usually chosen for setting are given in table 1.

Table 1.

Sodium chloride ($a_0 = 5{\cdot}628$ Å.U.)

Reflecting plane *hkl* (*n*) *	d_{hkl}/n
110 (2)	1·991
111 (2)	1·625
100 (4)	1·407
120 (2)	1·259
112 (2)	1·149
110 (4)	0·995
100 (6)	0·938

Typical crystallograms are shown in figure 7. These were taken with copper K_α radiation obtained from a Hilger-Shearer X-ray tube having a nickel-foil window and fed with about 5 mA. from a transformer working at a voltage of about 60 kV. r.m.s. A slit-width of 0·1 mm. was used, and the exposures given were in excess of that normally required so as to ensure better printed reproductions.

§ 7. THE CUBIC-CRYSTAL ANALYSER(13)

The cubic-crystal analyser has been constructed from consideration of the simple cube lattice as shown in figure 8 (1). This cube is taken as the fundamental basis of development of all other cubic structures which are encountered in crystallography, and which are obtained by the addition of lattice points in various symmetrical positions. Thus we get the body-centred cube, figure 8 (2), and the face-centred cube, figure 8 (3); but whatever the cubic structure, the measurement of the length a_0 offers a *unique specification of the substance undergoing investigation.*

a_0

---

* The values of (n) as given in column 1 have not been corrected to account for the internal structure of the elementary cube. See § 8.

The spacing of geometrically like planes parallel to the plane (*hkl*) is given by

$$d_{hkl} = a_0/(h^2 + k^2 + l^2)^{\frac{1}{2}} \qquad \ldots\ldots(5).$$

Now in practice with powder photographs it is found that the value of d_{hkl} is derived from a knowledge of the constants in the Bragg equation (1)

$$n\lambda = 2d_{hkl} \sin \theta,$$

provided of course that the order n of the spectrum considered is known. But this is not always determinable at sight, and hence solutions are found primarily for d_{hkl}/n.

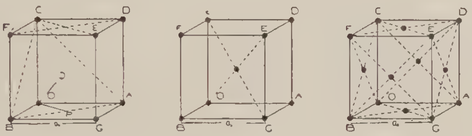

(1) (2) (3)

Fig. 8.

Rewriting equation (5) we get

$$d_{hkl}/n = a_0/n\,(h^2 + k^2 + l^2)^{\frac{1}{2}},$$

that is

$$a_0 = n\,(h^2 + k^2 + l^2)^{\frac{1}{2}}\,(d_{hkl}/n) \qquad \ldots\ldots(6).$$

Integral values being assigned to h, k, l and n, it has been possible to obtain a series of plots showing the linear relationship between a_0 and d_{hkl}/n for all the most probable crystal planes of reflections in various orders, 100 (1), 111 (3) etc. This was the simple process employed in the construction of the analyser, figure 9.

§ 8. ANALYSIS OF CUBIC CRYSTALLOGRAMS

The method used is applicable to crystal structures having cubic symmetry, and is similar to that employed by Hull and Davey[(14)] for determining the indices of the reflecting planes in hexagonal and tetragonal structures from graphical charts. A strip of paper is scaled off identically with that of the abscissae of the analyser. Values of d_{hkl}/n for the various powder lines recorded are read directly by means of the interplanar scale and then inscribed along one edge of the paper strip. The latter is then moved parallel to the horizontal axis with the zero mark always on the vertical (a_0) axis until a position is found where there is a full coincidence between the curves on the graphical plot and the markings on the paper strip. (Figure 9 demonstrates coincidence of lead lines.) The indices of the reflecting planes are read off directly, whilst the size of the unit elementary cube is obtained from the point of intersection of the strip edge with the vertical (a_0) axis.

The value of n given by the curves must not be confused with actual order of spectrum line obtained, since the analyser was constructed solely from considerations of the elementary unit cube without allowance for the internal distribution of the

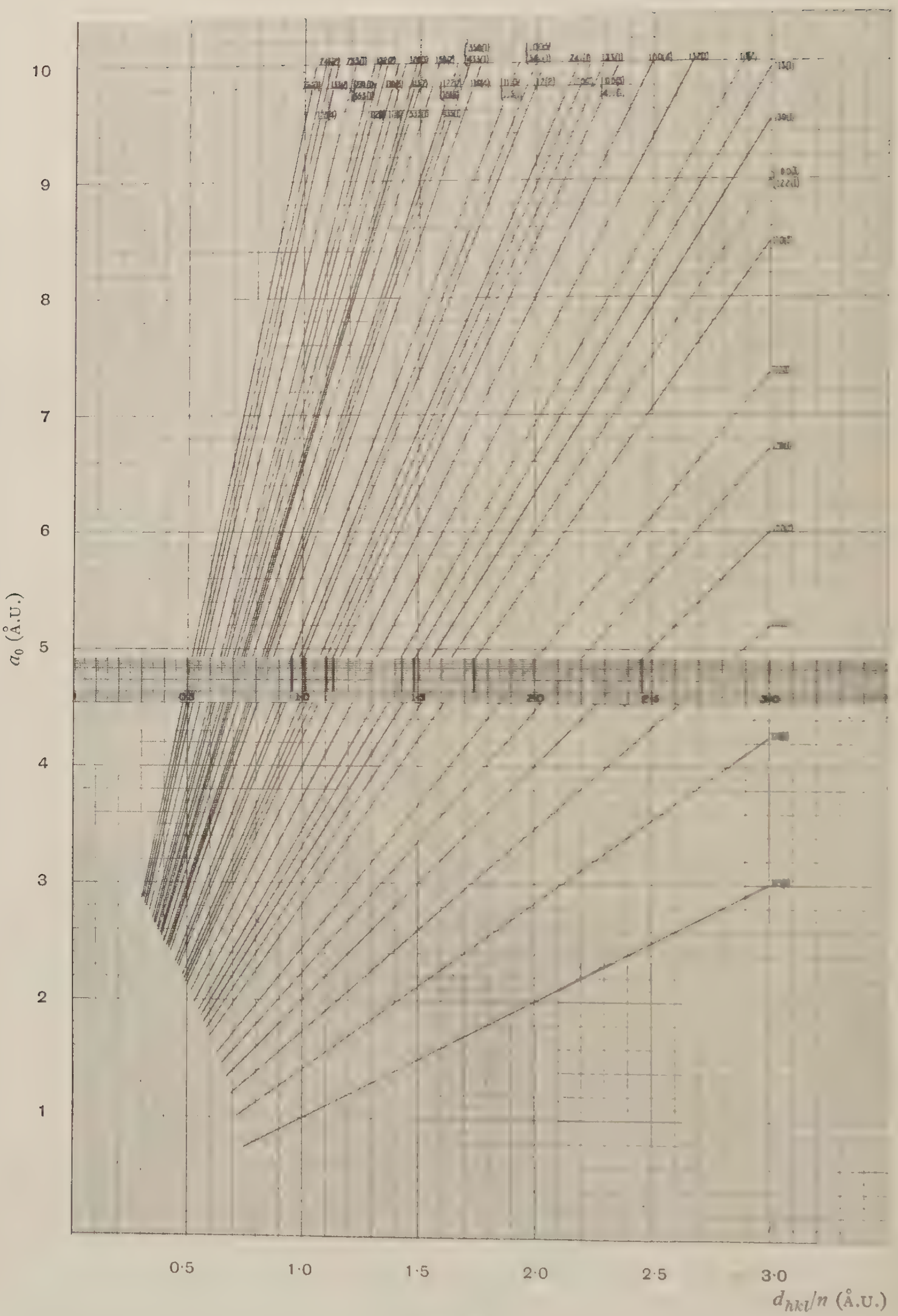


Fig. 9.

lattice points. This is by no means an objection to the use of the analyser, since it provides a method of identifying the various cubic structures by noting the different orders of reflection given by the analyser; for from a comparison of the interplanar distances of types of cubic structures indicated in figure 8, we obtain for the principal reflection planes (100), (110) and (111):

Elementary cube. $d_{100} = a_0;\ d_{110} = a_0/\sqrt{2};\ d_{111} = a_0/\sqrt{3}$ ......(7).

Body-centred cube (B–c). $d_{100} = a_0/2;\ d_{110} = a_0/\sqrt{2};\ d_{111} = a_0/2\sqrt{3}$ ......(8).

Face-centred cube (F–c). $d_{100} = a_0/2;\ d_{110} = a_0/2\sqrt{2};\ d_{111} = a_0/\sqrt{3}$ ......(9).

Thus from the above expression it can be seen that:

(i) d_{100} for the *B–c* and *F–c* structures is half that for the elementary cube. Hence first-order reflection for *B–c* and *F–c* structures from (100) planes will coincide with second-order reflection for an elementary cube; the second-order for *B–c* and *F–c* structures with fourth-order for elementary cube, and so on. Thus the analyser will not show any odd order reflections from (100) planes of *B–c* and *F–c* structures.

(ii) Similarly since d_{110} for *F–c* structures is half that for the elementary cube, no odd order reflections will be shown by the analyser for (110) reflections from *F–c* structures.

(iii) And since d_{111} for *B–c* structures is half that for the elementary cube, no odd-order reflections will be shown by the analyser for (111) reflection from *B–c* structures.

It is thus possible to formulate a double rule for distinguishing between *B–c* and *F–c* structures when the orders of the various reflections are read from the analyser.

Rule 1. If for 100 (n) and 110 (n) reflections odd values of n are missing, the structure is probably *F–c*.

Rule 2. If for 100 (n) and 111 (n) reflections, odd values of n are missing, the structure is probably *B–c*.

Once the structure is known, the correct value of n is determinable if required.

§ 9. PRACTICAL ILLUSTRATIONS

The analysis of crystallograms was quickened by use of a special *T*-square which obviated the necessity for transferring readings of d_{hkl}/n on to a strip of paper. This *T*-square was fitted with a celluloid scale which was an exact replica of and coincident with the d_{hkl}/n scale of the graphical plots. Moving steel pointers were provided for setting to the readings of the powder lines, and the point of coincidence was found by moving the *T*-square along the edge of a drawing-board upon which the analyser was mounted.

Table 2. Lead filings (figure 7 G).

Spacing given by interplanar scale d_{hkl}/n (Å.U.)	Reflection plane given by analyser *hkl* (*n*)
1·74	110 (2)
1·481	113 (1)
1·422	111 (2)
1·23	100 (4)
1·133	133 (1)
1·103	120 (2)
1·015	112 (2)
0·956	111 (3)

Possible planes missing include 100 (3), 110 (3), 100 (5). Full coincidence was obtained at a_0 = 4·92 Å.U. Result of analysis: *F–c* structure, a_0 = 4·92 Å.U.

Table 3. Tungsten filings (figure 7 F).

Spacing given by interplanar scale d_{hkl}/n (Å.U.)	Reflection plane given by analyser *hkl* (*n*)
2·22	110 (1)
1·58	100 (2)
1·29	112 (1)
1·12	110 (2)
1·008	130 (1)
0·918	111 (2)

Possible planes missing include 100 (3), 111 (1). Full coincidence was obtained at a_0 = 3·16 Å.U. Result of analysis: *B–c* structure, a_0 = 3·16 Å.U.

§ 10. CONCLUSION

The instrument here described simplifies the technique of X-ray crystallography. Owing to the focussing action, the time of exposure can be decreased to such a value that the utility of X-rays for commercial analysis is enhanced. The interplanar scale eliminates hours spent in calculation, and in combination with the cubic-crystal analyser enables a complete analysis of most substances having a cubic structure to be made in less than 10 minutes. The accuracy of the method is greatly dependent upon the accuracy of the machining of the instrument. But if the instrument is calibrated by taking an exposure of some standard substance of known lattice spacings, analysis can be made quite easily with errors less than 1 in 400.

REFERENCES

(1) SEEMAN, H. *Ann. der Phys.* **59**, 455 (1919).
(2) BOHLIN, HELGE. *Ann. der Phys.* **61**, 421, 424 (1920).
(3) BRAGG, W. H. and BRAGG, W. L. *X-Ray and Crystal Structure*, London (1915).
(4) DEBYE, P. and SCHERRER, P. *Phys. Zeit.* **17**, 277 (1916).
DEBYE, P. and SCHERRER, P. *Phys. Zeit.* **18**, 291 (1917).
(5) HULL, A. W. *Phys. Rev.* **10**, 661 (1917).
(6) WEISS, H. *Proc. R.S.* A, **108**, 643 (1925).
(7) PAULI, O. *Zeit. f. Kryst.* **56**, 591 (1921).
(8) BIJL, A. J. and KOLKMEYER, N. K. *Proc. Section of Sciences, Koninklijke Akademie van Wetenschappen at Amsterdam*, **21**, 494 (1919).
(9) DAVEY, W. P. *Gen. Elec. Rev.* **25**, 565 (1922).
(10) WYCKOFF, R. W. G. *Zeit. f. Kryst.* **59**, 55 (1923).
(11) MÜLLER, A. *Phil. Mag.* **42**, 419 (1921).
(12) WYCKOFF, R. W. G. *The Structure of Crystals*, New York (1924).
(13) ADAM HILGER, LTD. *The Cubic Crystal Analyser*. (Descriptive booklet.)
(14) HULL, A. W. and DAVEY, W. P. *Phys. Rev.* **17**, 549 (1921).

ELECTRO-ENDOSMOSIS AND ELECTROLYTIC WATER-TRANSPORT. PART II

By H. C. HEPBURN, Ph.D.,
Birkbeck College

Received February 7, 1931. *Read June* 5, 1931.

ABSTRACT. A new and convenient form of apparatus is described for the measurement of liquid-transport produced by the application of an electric field across a diaphragm of parchment paper. Results obtained with solutions of copper sulphate over the concentration range 0·0005-normal to 1-normal are compared with corresponding results obtained previously, by the author, with a diaphragm of powdered glass. The liquid-transport per faraday with the parchment diaphragm decreases strongly with increasing concentration up to 0·2-normal, but maintains practically a constant value over the concentration range 0·4-normal to 1-normal. This value is compared with that deduced for the electrolytic water-transport per faraday from the values of the experimental Hittorf transport number; and evidence is adduced indicating that there is no increase in the electrolytic water-transport per faraday with decreasing concentration from 0·4-normal. The data for the solutions over the concentration range 0·0005-normal to 0·2-normal appear to be consistent with the hypothesis of a composite effect produced by a constant electrolytic water-transport per faraday (of the same magnitude as the observed transport per faraday over the concentration range 0·4-normal to 1-normal) and by a specific (electro-endosmotic) action of the parchment diaphragm. The determination of electrolytic water-transport is utilized to correct the values of the experimental Hittorf transport number obtained from the data of Hittorf and Metalka. The true transport number in the case of copper sulphate solutions decreases with decreasing concentration from 1-normal, but the values at concentrations 0·125-normal and less appear to be little different from that at infinite dilution.

§ 1. INTRODUCTION

The flow of liquid in electro-endosmosis appears to be determined by the movement of the free ions of the electrical double layer formed, according to the classical theory*, at the interface diaphragm-aqueous solution†. In the case of a diaphragm of powdered glass and aqueous solutions of copper sulphate, the author showed in a former paper‡ that the number of free ions (as indicated by their charge) decreased strongly with increasing concentration of electrolyte; at concentrations above 0·005-normal no free charge could be detected. The liquid-transport per constant applied voltage across the diaphragm also decreased strongly with increasing concentration, but there was still a considerable flow at concentration

---

* Helmholtz, *Wied. Ann.* **7**, 337 (1879).

† See J. O. W. Barratt and A. B. Harris, *Biochem. J.* **6**, 315 (1912); and J. W. McBain, *Trans. Faraday Soc.* **16** (Appendix), 150 (1920).

‡ H. C. Hepburn, *Proc. Phys. Soc.* **39**, 99 (1927).

0·005-normal; and over the concentration range 0·005-normal to 0·5-normal the rate of flow per constant applied voltage was not appreciably changed.

In view of the evidence adduced as to the neutralization of the free charges of the diaphragm, it was concluded that electro-endosmosis ceased to play a prominent part at concentration 0·005-normal. The liquid-transport per faraday over the concentration range 0·005-normal to 0·1-normal showed a linear relation, when plotted against dilution, similar to that given by the data of Remy* for aqueous solutions of potassium chloride with a parchment diaphragm; and the suggestion was made that the data for the copper sulphate solutions of concentrations 0·005-normal and above appeared to be characteristic of electrolytic water-transport, i.e. of the water-transference which occurs during the ordinary process of electrolysis. This suggestion was based largely on the conclusion of Remy† and others that parchment paper appears to form a suitable partition for the measurement of electrolytic water-transport.

It seemed desirable, in order to confirm the above suggestion, to obtain data for the transport in the case of a parchment diaphragm and aqueous solutions of copper sulphate. The present work is devoted to this end; and the question of the electrolytic water-transport is further investigated. A new and convenient form of apparatus of considerably greater sensitivity than that of the earlier apparatus has been devised, and a more precise regulation of working temperature has been secured by immersion of the apparatus in an electrically heated water-bath with thermostatic control.

§ 2. THE APPARATUS

The apparatus was constructed mainly from hard glass tubing, 3 cm. in diameter. The two tubes *A*, *A′*, figure 1, each 14 cm. long, carried side-pieces *B*, *B′*. The extremities of the side-pieces were formed into projecting flanges, the surfaces of which were ground to fit one another. The cup-like bases of the tubes *A*, *A′* served to collect any insoluble products of electrolysis formed at the electrodes, e.g. the black colloidal substance formed at the cathode in the case of the more dilute solutions of copper sulphate. A capillary tube *C′*, about 25 cm. long, was joined to the tube *A* at *C*; the capillary was approximately 1 mm. in diameter, calibration with a thread of mercury giving the volume per cm. as 0·01127 cm.^{3} The tube *A* was widened slightly at the top to carry the hollow glass stopper *D*, the surfaces of contact being ground to provide a good joint. The tube *E* was joined to the lower end of the stopper and the short tube *F* to the upper part, the ends of both tubes being open and permitting a length of wire to be passed through the stopper.

The electrodes, which consisted of lengths of electrolytic copper wire (1 mm. in diameter) wound into the form of flat spirals with straight projecting pieces about 11 cm. long, were practically identical with those employed in the previous work‡. The straight piece of one length of wire was passed through the tube *E* of the stopper until it emerged at *F*, leaving the spiral projecting from the end of *E*. The wire was then cemented into the tube *E* with Faraday cement, the position of the spiral being regulated so that its centre lay in the axis of the side tube *B* when the stopper was in position. The stopper was finally turned to bring the plane of the spiral normal to the axis of the tube *B*, and the position was recorded by means of scratches on the stopper and on the adjacent part of the tube *A*. A similar electrode in the tube *A′* was carried by the stopper *G*. This stopper was pierced with holes so as to leave *A′* open to the air.

---

* *Z. Elektrochem.* **29**, 365 (1923).

† *Loc. cit.*

‡ H. C. Hepburn, *loc. cit.*

The use of a stopper, in place of a tap, to close the tube *A* facilitates the filling and emptying of the apparatus, at the same time providing a convenient means of introducing the electrode which may readily be removed for cleaning. It is possible, moreover, as explained later, to dispense with a lubricant at the joint, the risk of contaminating the solution being thus avoided.

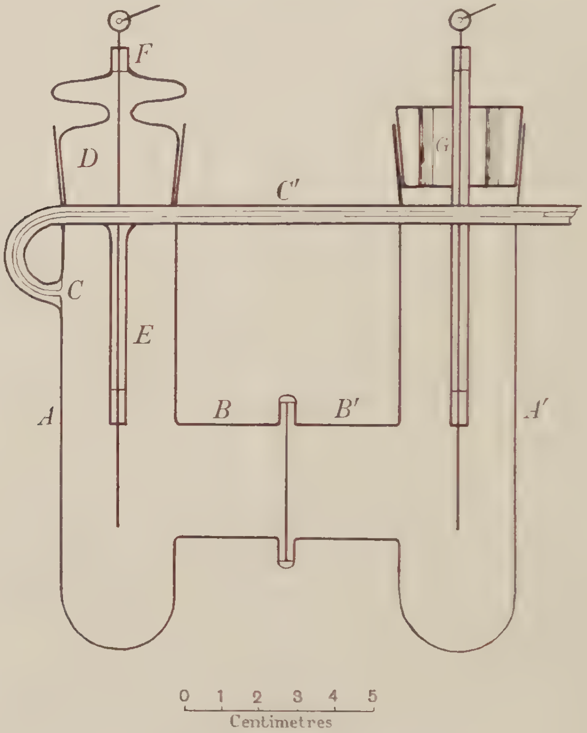


Fig. 1. The apparatus.

The diaphragm consisted of a disc of parchment paper large enough to cover the projecting flange of the tube *B* or *B′*. The disc, after examination to ensure freedom from flaws and pinholes, was wetted with distilled water and placed over the flange of the tube *B*. The two flanges were then brought together by means of stout rubber bands which were passed round the tubes *A*, *A′*; and the projecting edge of the parchment disc (representing the expansion on wetting) was cut off with a sharp knife. Hot molten dental (sticky) wax was then applied to the joint of the two flanges; the two parts of the apparatus thus being cemented together, the flanges holding the parchment disc tautly in position. Dental wax was adopted after trials with several cements; it was found to provide a strong and waterproof joint, at the same time eliminating the possibility of electrical leaks at the joint—a frequent source of trouble*—when the apparatus was placed in the water bath.

§ 3. EXPERIMENTAL

After the fixing of the parchment diaphragm the apparatus was at once filled with the most dilute copper sulphate solution (0·0005-normal) in the range selected (0·0005-normal to 1-normal), a long-stemmed funnel being used for this purpose to avoid the introduction of air bubbles. The process of filling and emptying the apparatus was several times repeated, a quantity of solution being allowed to flow through the diaphragm under a hydrostatic pressure head. After the final filling the stopper D was placed in position, care being taken to avoid the formation of air bubbles under the stopper. The channel between the stopper and the top of the tube A was dried with filter paper and then filled with rubber solution. Finally the level of the solution in the tube A' was adjusted to that of the capillary, and the apparatus clamped in a thermostat tank of capacity 50–60 litres. The apparatus was allowed to remain in the tank for 24 hours to ensure equilibrium between the diaphragm and solution, a coating of rubber meantime forming over the stopper and providing an airtight joint.

As a preliminary to the measurement of liquid-transport the apparatus was tilted to deliver drops from the capillary tube, until finally, when the capillary was restored to the horizontal, the liquid ran back to a point in the tube. The subsequent movement of the meniscus when an electric field was applied at the electrodes furnished a measure of the liquid-transport through the diaphragm†.

A rigorous cleansing of the capillary was found to be necessary to avoid the tendency of the meniscus to cling to the walls of the tube. The tube was treated first with benzene and then with alcohol, and finally was allowed to dip into a mixture of chromic and nitric acids for some days. Further subsequent treatment with hot chromo-sulphuric acid was needed also in the intervals between the flow measurements.

Preliminary experiments showed that the meniscus, after coming practically to rest after the delivery of drops from the capillary tube, began to move slowly towards the end of the tube. This "slow" flow, the magnitude of which was found to depend on the mechanical resistance of the diaphragm, was evidently produced by a small pressure-head developed in the apparatus. The flow through the diaphragm due to the application of an electric field at the electrodes was taken as the difference between the observed flow when the field was applied and the "slow" flow previously observed.

The experimental method adopted was to bring the meniscus initially to or below the point 4·00 cm. on the engraved scale attached to the capillary tube. The meniscus, after traversing at least 1 cm. of the tube, was then timed by stop watch over the half-centimetre from 5·50 to 6·00, a lens being used in this and the following measurement to locate accurately the positions on the scale. The current, which was derived from a battery of storage cells, was switched on immediately the meniscus had passed the point 6·00, and the time taken to traverse the centimetre from 7·00 to 8·00 observed; the time for the half-centimetre 7·00 to 7·50 also was observed, but without the stop watch being stopped. The velocity of liquid-transport due to the applied electric field was taken as the difference between the rate of flow over the length 7·00 to 8·00 and that over the length 5·50 to 6·00. (N.B. The rate of "slow" flow was found by preliminary experiment to be practically uniform over the length 5·50 to 8·00 of the capillary.)

---

* See F. Fairbrother and H. Mastin, *J. Chem. Soc.* **125**, 2322 (1924).

† Cf. J. Perrin, *J. Chim. phys.* **2**, 617 (1904).

Measurements of liquid-transport were made with the solutions in order of increasing concentration, the procedure indicated in the preceding paragraphs being followed. At each concentration the rate of flow for the half-centimetre 7·00 to 7·50 was compared with that for the next half-centimetre 7·50 to 8·00, the determination being rejected if a difference greater than 2 per cent. was disclosed; in actual practice the difference rarely exceeded 1 per cent. In the event of the difference exceeding 2 per cent. the apparatus was refilled with fresh solution and the measurement repeated after the apparatus had remained in the thermostat tank for a further period of 24 hours. Successive determinations also were made, as described, to confirm that results could be reproduced.

The method described for applying a test of consistency, in preference to repetition of the measurement without change of solution, was adopted in view of the earlier work of the author which indicated that a progressive disturbance in the rate of liquid-transport, possibly as the result of concentration changes, etc. in the region of the electrodes, often arises when a measurement is several times repeated or when the current from the battery is repeatedly reversed. In view of the possibility of such disturbance the time of observation was reduced to a minimum, and the electrodes were placed at some distance from the diaphragm.

The mean current through the diaphragm was obtained from observations made with the meniscus at the beginning and end respectively of the timed centimetre; no appreciable variation in the current was, however, observed during the transit. The current value at a given concentration was approximately the same as that with the powdered-glass diaphragm, e.g. 0·3367 amp. with the parchment diaphragm and 0·3140 amp. with the powdered-glass diaphragm in the case of normal copper sulphate solution.

In order to ensure that there was no thermometric effect due to a change in temperature during the course of a flow-measurement the thermostat tank was heavily lagged with felt, and the water surface of the tank covered with a layer of B.P. paraffin to minimize heat losses through evaporation. The tank temperature was controlled within a limit of ± 0·1° C. by means of an electrical device similar to that described by Clack and Jarvis*; matters being so arranged, to avoid thermometric effects, that no heat was supplied to the tank immediately before or during the course of the flow-measurements. As certain of the observations were made in the summer months, it was not practicable to adopt a uniform working temperature of 18° C., and the determinations of liquid-transport at concentrations 0·0005-normal to 0·2-normal were made at temperatures in the range 18·4° C. to 21·4° C. Control experiments with solutions of these concentrations indicated, however, that the variation in the liquid-transport per faraday over the temperature range 18·0° C. to 21·4° C. is less than the limit of experimental error (between 1 and 2 per cent.) in the flow-measurements. The measurements over the concentration range 0·4-normal to 1-normal were made at temperatures within 0·1° C. of 18·0° C.

---

* *J. Sci. Inst.* **4**, 330 (1927).

A thermometric action arises in consequence of the heating effect of the current on the solution between the electrodes. The energy developed between the electrodes, which is almost completely liberated in the form of heat, is proportional (per unit time) to the product of the current and the applied voltage. In the flow-measurements already described a constant voltage was applied over the whole range of concentrations investigated, the thermometric action due to the heating effect of the current being practically constant when expressed as a flow per faraday. The magnitude of the correction was determined by means of control experiments in which the liquid-transport was measured with the current in the reverse direction from that previously adopted, correction being made for the "slow" (gravitational) movement referred to earlier. The thermometric action, which had previously assisted, then opposed the flow, the correction being given by half the difference between the two corresponding values of the liquid-transport per faraday. Measurements with 0·01-normal and 1·0-normal solutions gave the values 41·0 and 40·4 respectively for the heating correction in cm.^{3}/faraday. These values are in satisfactory agreement, and a mean correction of 40·7 cm.^{3}/faraday has been adopted. The correction of 40·7 cm.^{3} gives a value of 30·0 cm.^{3}/faraday as the true liquid-transport with normal solution. In order to confirm this value, further measurements similar to those already described, but in which a lower current value (0·0993 amp. in place of 0·3367 amp.) was adopted, were made with normal solution. The values obtained in two sets of measurements for the true liquid-transport per faraday were 30·8 cm.^{3} and 30·4 cm.^{3} respectively, which are in satisfactory agreement with the value (30·0 cm.^{3}) relating to a current of 0·3367 amp.

The direction of liquid-transport throughout the whole range of concentrations investigated was from anode to cathode as in the case of the powdered-glass diaphragm.

§ 4. RESULTS AND CONCLUSIONS

The experimental results are given in table 1. $1/T_m$ (reciprocal seconds) is the reciprocal of the observed time of liquid-transport per 1 cm. of the capillary tube, less the correction $1/T_s$, T_s being the time of "slow" flow per cm. for the gravitational movement. The liquid-transport in cm.^{3}/faraday (v_f) is calculated from the expression $[(1/T_m)\,(1/I_m)\,(0{\cdot}01127)\,(96{,}540)] - [40{\cdot}7]$, I_m being the mean current

T_m

through the diaphragm in amperes, and 0·01127 the volume of the capillary in cm.^{3} per cm. The deduction of 40·7 cm.^{3} represents the correction for the heating effect of the current referred to in § 3. The values obtained by the author* for the liquid-transport per faraday in the case of the powdered-glass diaphragm and solutions of copper sulphate are added for purposes of comparison.

Comparison of results with diaphragms of parchment and of powdered glass. It will be seen from table 1, columns 4 and 5, that the values of the liquid-transport per faraday with the powdered-glass diaphragm are considerably greater than those with the parchment diaphragm, even over the concentration range 0·005-normal to 0·5-normal; and if we conclude that the parchment diaphragm exerts only a small influence on the liquid-transport‡ it seems necessary to postulate a specific action of the powdered-glass diaphragm on the flow at concentrations of 0·005-normal or more. In view, however, of the evidence adduced in the former paper as to the neutralization of the free charge of the powdered-glass diaphragm at a concentration approaching 0·005-normal, no material part of the liquid-transport obtained with further increase in concentration can apparently be attributed to electro-endosmosis in the sense of the surface phenomenon discussed by Helmholtz§; the action of the diaphragm then appears to be mainly of a mechanical rather than electrical character. The author hopes to pursue this question further in a subsequent investigation.

Table 1.

Concentration of $CuSO_4$ (gm.-equiv./litre)	Mean current I_m (amp.)	Reciprocal $1/T_m$ of time of flow per cm.	Liquid-transport v_f (cm.^{3}/faraday)	Liquid-transport v_f (cm.^{3}/faraday)
	Parchment diaphragm	Parchment diaphragm	Parchment diaphragm	Powdered-glass diaphragm
0·0005	·000684	·001412	2201	324100
0·001	·001484	·002054	1464	202500
0·002	·002549	·002884	1190	72100
0·005	·00572	·004363	789	18340
0·01	·01049	·005252	504	9320
0·014	·01380	·005752	413	—
0·02	·01848	·006131	320	4754
0·03	·02524	·006397	235	—
0·05	·03705	·006066	137	2276
0·1	·0654	·007076	76·9	1238
0·2	·1070	·007823	38·8	680
0·4	·1845	·01198	29·9	—
0·5	·2113	·01356	29·1	330
0·6	·2465	·01570	28·5	—
0·8	·2860	·01837	29·1	—
1·0	·3367	·02189	30·0	†

† No perceptible flow obtained. (N.B. The apparatus employed was not designed for the measurement of slow rates of flow.)

---

* H. C. Hepburn, *loc. cit.*

‡ This question is further considered below (page 534).

§ *Loc. cit.*

The relation between the liquid-transport per faraday and the dilution of the electrolyte in the case of the parchment diaphragm and the solutions of copper sulphate is shown graphically in figure 2. The apparent discontinuity between dilutions 10 and 20 (see figure 2 *A*) is considered below (page 534).

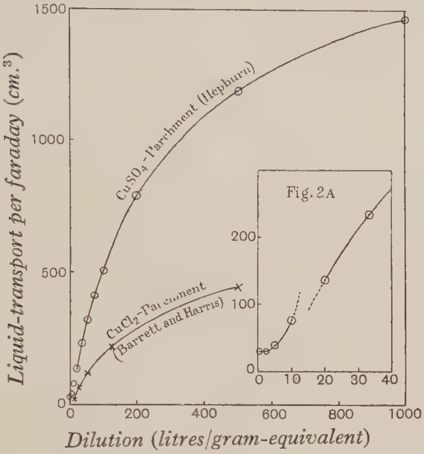


Fig. 2. Liquid transport per faraday (N.B. An enlargement of the lower part of the $CuSO_4$-parchment curve appears in Fig. 2*A*).

The values of the liquid-transport per faraday over the dilution range 20 to 1000 lie satisfactorily on a smooth curve, though the value for dilution 2000 lies above the extension of the curve; but there is no linear relation as in the case of the powdered-glass diaphragm and copper sulphate solutions of dilutions 10 to 200 or of the parchment diaphragm and potassium chloride solutions of dilutions 10 to 100 employed by Remy*. A curve of type similar to that relating to the parchment diaphragm and the copper sulphate solutions of dilutions 20 to 1000 is given, however (see figure 2), by the data of Barratt and Harris† for a parchment diaphragm and cupric chloride solutions; the values of the liquid-transport per faraday in the latter case are lower than those relating to the copper sulphate solutions. A result similar to that found with the powdered-glass diaphragm has been obtained by Boutaric and Doladilhe‡ in measurements of liquid-transport through a porous pot in the case of copper sulphate solutions of dilutions 100 or less. Boutaric and Doladilhe report that the liquid-transport is proportional to the current and to the electrolyte dilution; the data for the powdered-glass diaphragm over the dilution range 100 to 200 lead to approximately the same result.

Bearing of the data obtained with the parchment diaphragm on the electrolytic water-transport and comparison with other data. It is evident that in migration experiments where a parchment partition is interposed in the current path, as in the present work and in the work of Remy and others, the results will not give a satisfactory indication of the electrolytic water-transport unless the specific influence of the parchment partition on the liquid-transport can be neglected.

---

* *Loc. cit.* † *Z. Elektrochem.* **18**, 221 (1912). ‡ *Compt. Rend.* **187**, 1142 (1928).

The work of Bein* and Hittorf† indicates that a parchment diaphragm is of little influence, especially with solutions of the alkali salts. Remy‡ and Baborovsky§ have recently concluded, however, that even with parchment the specific influence of the diaphragm cannot in general be neglected at concentrations below normal. Baborovsky‖ has attempted to apply a correction for the diaphragm effect, but without success.

It thus appears to be desirable, in order to obtain some confirmation of the estimates of electrolytic water-transport given by the results of the parchment diaphragm method, to make a comparison with the results of an independent method. This has been effected with fairly satisfactory results in the case of normal solutions of hydrochloric acid and of certain alkali chlorides by means of the Nernst method of indifferent reference-substance¶. Comparison over an extended range of concentration is not, however, possible, as determinations by the indifferent-reference-substance method have only been carried out at comparatively high concentration. Moreover, no comparison is practicable in the case of solutions of the copper salts owing to the difficulty in finding a suitable reference-substance which would not interact with the $Cu^{\cdot\cdot}$ ion. A similar difficulty arises when we attempt to find a basis of comparison in the results of an indirect method, such as that of distribution**.

In view, however, of the general conclusion of Remy and Baborovsky††, which is based on results obtained with solutions where independent confirmatory evidence is available as to the magnitude of the electrolytic water-transport, it seems probable that the specific (electro-endosmotic) effect of the parchment diaphragm may be neglected in the case of normal copper sulphate solution. It will be observed, moreover (see table 1) that the liquid-transport per faraday maintains practically a constant value over the concentration range 0·4-normal to 1-normal, but decreases strongly with increasing concentration (a characteristic of electro-endosmosis) in the case of concentrations below 0·4-normal. This latter result suggests that the specific effect of the parchment diaphragm may be neglected in the case of solutions of 0·4-normal and higher concentrations.

The mean value of the liquid-transport per faraday (29·3 cm.$^3 \equiv$ 1·63 mols) over the concentration range 0·4-normal to 1-normal is considerably less than that (4·10 mols) deduced for the electrolytic water-transport per faraday from the values of the experimental Hittorf transport number. The calculation from the values of the Hittorf transport number is based on the relation $x = dn/dc$, deduced by Riesenfeld and Reinhold‡‡ from equation (1) on page 535, x being the electrolytic water-trans-

x

---

* *Z. Phys. Chem.* **28**, 439 (1898).

† *Ibid.* **39**, 613 (1902); **43**, 237 (1903).

‡ *Trans. Faraday Soc.* **23**, 383–385 (1927).

§ *Z. Phys. Chem.* **129**, 129 (1927); *Coll. Czech. Chem. Comm.* **1**, 315 (1929).

‖ *Loc. cit.*

¶ See H. Remy, *Trans. Faraday Soc.* **23**, 382, 383 (1927).

** See J. N. Sugden, *J. Chem. Soc.* 174 (1926).

†† *Loc. cit.*

‡‡ *Z. Phys. Chem.* **66**, 672 (1909).

port in mols per faraday, n the Hittorf transport number, and c the concentration in equivalents per mol. The difference between the two results appears to be due to the fact that the true transport number is not independent of concentration as required by Riesenfeld and Reinhold's expression for x. This question is further considered on p. 535. n, c

Dependence of the electrolytic water-transport per faraday on the electrolyte concentration. The electrolytic water-transport per faraday has been shown to be dependent on the transport numbers and the difference in the hydration of the anions and cations of the electrolyte*. The ionic hydration may be considered as including also the water which is carried along by the ions in consequence of the frictional forces due to (i) the impact of the ions on the surrounding water molecules†, and (ii) the electrophoresic effect of the so-called ionic atmosphere‡.

Taylor and Sawyer§ have pointed out that notwithstanding the divergent estimates of the actual number of water molecules associated with or influenced by any specific ion, the opinion seems to prevail that this number is only slightly, if at all, influenced by concentration. In the general case of solutions of the sulphates, however, the distribution-measurements of Sugden‖, made over the concentration range 2-normal to 0·1-normal, indicate some diminution in the associated water with decreasing concentration; but this result must apparently be accepted with reserve in view of the secondary actions, such as that of depolymerizing action on the solvent, probably associated with the method of distribution.

The true transport number of the anion in the case of copper sulphate solutions of concentrations 1-normal and below appears to diminish with decreasing concentration (see page 536). This effect, corresponding to an increase in the transport number of the cation, would tend to increase the liquid-transport (which is directed towards the cathode) and to oppose the effect of diminution in the magnitude of the associated water suggested by the results of Sugden. The resultant action, viewed in relation to the observed liquid-transport per faraday over the concentration range 1-normal to 0·4-normal, appears to produce little variation in the magnitude of the electrolytic water-transport per faraday. At 0·125-normal or lower concentrations the values of the true transport number appear to be little different from that relating to infinite dilution, the general evidence then pointing to a constant or slightly diminishing value of the electrolytic water-transport per faraday with decreasing concentration.

Further evidence regarding the dependence of the electrolytic water-transport per faraday on the concentration may be adduced from a consideration of the linear relation between the Hittorf transport number and the concentration, referred to on page 536. Comparison with equation (1) shows that the linear relation, which holds over the concentration range 1-normal to 0·0212-normal*, leads to a constant value for the electrolytic water-transport per faraday, if—as seems probable (see page 536)—the true transport number also is related to concentration by a linear law. The electrolytic water-transport x per faraday is then given by the difference between the slopes $(dn/dc - dw/dc)$ of the two straight lines representing respectively the Hittorf transport number and the true transport number.

---

* See W. Nernst, *Theoretical Chemistry*, p. 447 (1923).

† Cf. F. A. Lindemann, *Z. Phys. Chem.* **110**, 394 (1924). Cf. H. Remy, *Trans. Faraday Soc.* **23**, 385 (footnote) (1927).

‡ P. Debye and E. Hückel, *Phys. Z.* **24**, 305 (1923). Cf. H. Remy, *Trans. Faraday Soc.* **23**, 385 (footnote) (1927).

§ *J. Chem. Soc.* 2095 (1929).

‖ *Loc. cit.*

The specific effect of the parchment diaphragm. In view of the conclusion of the preceding paragraphs, the regular increase in the liquid-transport per faraday with decreasing concentration from 0·4-normal, observed in the present work, must evidently be attributed to the specific effect of the parchment diaphragm. If, as a first approximation, we assume that the electrolytic water-transport per faraday is independent of concentration and equal in magnitude to the observed transport per faraday over the concentration range 1-normal to 0·4-normal, we obtain the expression $(v_f - 29{\cdot}3)$ for the part of the transport attributable to the specific effect v_f of the parchment diaphragm, v_f being the observed transport per faraday.

The diaphragm effect is usually measured in terms of the liquid-transport produced by the application across the diaphragm of a constant potential difference. If the specific conductivity within the diaphragm is no different from that in the bulk of the solution, the liquid-transport for a constant applied potential difference λ across the diaphragm is proportional to $(v_f - 29{\cdot}3)\,\lambda$, λ being the specific conductivity of the electrolyte solution. Some disturbance in the specific conductivity may be produced by the following possible factors: (i) diaphragm-surface current†, and (ii) change in the ionic mobilities whilst the ions are passing through the diaphragm‡; but in view of the comparatively inactive character of parchment paper when employed as diaphragm material, it is probable that the factors mentioned may be neglected for our present purposes without the introduction of any appreciable error.

Values of $v_f\lambda$ and of $(v_f - 29{\cdot}3)\,\lambda$ are shown graphically in figure 3; the values of λ have been obtained from the data of Kohlrausch. It will be seen that the curve relating to $v_f\lambda$ shows an apparent discontinuity between concentrations 0·05-normal and 0·1-normal (see also figure 2 *A*), but the curve relating to $(v_f - 29{\cdot}3)\,\lambda$ appears to be continuous. This latter curve, representing the specific effect of the parchment diaphragm, passes through a pronounced maximum and is of the same characteristic shape as that met with in certain cases where the diaphragm effect is predominant, e.g. with dilute solutions of hydrochloric acid in a powdered-glass diaphragm§.

The present data thus appear to be consistent with the hypothesis of a composite effect produced by a constant electrolytic water-transport per faraday and by a specific action of the parchment diaphragm, the latter action apparently becoming negligible at a concentration between 0·2-normal and 0·4-normal.

Determination of true transport number. It has been pointed out by Riesenfeld and Reinhold* and others that the values obtained for the transport numbers of ions in solution by the Hittorf method† require correction in consequence of concentration-changes in the neighbourhood of the electrodes, produced by the electrolytic water-transport. The present determination of electrolytic water-transport provides a basis for this correction.

---

* No data appear to be available for the Hittorf transport number in the case of concentrations below 0·0212-normal.

† Cf. H. C. Hepburn, *Proc. Phys. Soc.* **39**, 102 (1927).

‡ Cf. A. A. Green, A. A. Weich and L. Michaelis, *J. Gen. Physiol.* **12**, 473 (1929).

§ See H. C. Hepburn, *Proc. Phys. Soc.* **38**, 363 (1926).

In the case of solutions of copper sulphate, where the direction of electrolytic water-transport is from anode to cathode, the following relation between the experimental Hittorf transport number and the true transport number is given by Riesenfeld and Reinhold:

$$w = n - cx \qquad (1).$$

Here w is the true transport number, n the experimental Hittorf transport number, w, n
c the electrolyte concentration in equivalents per mol, and x the electrolytic water- c, x
transport in mols per faraday. The symbols w, n refer to the anion, the corresponding numbers for the cation being $1 - w$, and $1 - n$.

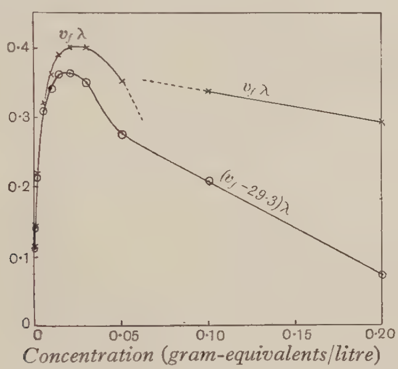


Fig. 3. Liquid transport per constant applied voltage across the diaphragm.

The data available for the experimental Hittorf transport number in the case of copper sulphate solutions over the concentration range 0·08-normal to 2-normal are conveniently shown in graphical form by Riesenfeld and Reinhold‡. The most regular results over the concentration range 0·3-normal to 2-normal appear to be those of Hittorf § (determinations at normalities 1·96, 1·34, 0·712, and 0·327; temperature of determinations 4°–6° C.), the plot of his values occupying roughly a mean position relative to the plots of the other data. Hittorf's values for concentrations below 0·327-normal are somewhat irregular. Metalka ||, working at a temperature of 18° C., obtained the value 0·672 for the Hittorf transport number with solutions of concentrations 0·49-normal and 0·25-normal. This value is somewhat higher than that (0·659) obtained for concentration 0·5-normal by large-scale

---

* *Loc. cit.* † W. Hittorf, *Pogg. Ann.* **89**, 177 (1853) *et seq.*

‡ *Loc. cit.* N.B. No later data appear in the Landolt-Börnstein *Tabellen* (1923 and 1927).

§ *Pogg. Ann.* **89**, 177 (1853).

|| H. Jahn and collaborators, *Z. Phys. Chem.* **37**, 673 (1901).

graphical interpolation of Hittorf's data, but Metalka's values relating to 0·164-normal and lower concentrations lie satisfactorily on the continuation of the plot of Hittorf's data relating to the concentration range 1·96-normal to 0·327-normal. Metalka does not record a measurement with 1-normal solution, but interpolation of Hittorf's data gives the value 0·695 as against 0·69 obtained by Kermis* at room temperature.

The above analysis suggests that the magnitude of the transport number is not greatly dependent on the temperature within the limits 4° C. to room temperature. In this connexion it is pointed out that Hittorf† obtained the value 0·713 for the transport number with 1·34-normal copper sulphate solution at room temperature (18°–21° C.) as against 0·712 at 5·5° C., and he concluded that there was no temperature effect within the limits 4°–21° C.

The values given in table 2 for the Hittorf transport number appear to be the most probable of the available results (see the foregoing analysis) and are taken from the data of Hittorf (1-normal to 0·327-normal) and of Metalka (0·1639-normal to 0·0212-normal‡). The solution density data in the Landolt-Börnstein *Tabellen* have been used to obtain the concentration values in equivalents per mol.

Table 2.

Concentration of $CuSO_4$ (gm.-equiv./litre)	Concentration (gm.-equiv./mol)	Hittorf transport number n	True transport number w
1·0	0·01806	0·695	0·666
0·712	·01285	·675	·654
·5	·00902	·659	·644
·327	·00590	·645	(·635)
·1639	·00296	·634	(·629)
·125	·00225	·627	(·623)
·0833	·00150	·626	(·624)
·0625	·00113	·624	(·622)
·0419	·00076	·625	(·624)
·0306	·00055	·625	(·624)
·0254	·00046	·625	(·624)
·0212	·00038	·625	(·624)

The values of the Hittorf transport number n in table 2 are related, within close limits, to the concentrations in equivalents per mol by a linear law, the mean deviation being less than 0·1 per cent. of the linear value; the maximum deviation is 0·63 per cent., and the deviation at the lowest concentration 0·24 per cent. The values of the true transport number w in the case of concentrations 1-normal, 0·712-normal and 0·5-normal have been calculated by means of equation (1), the mean value of 1·63 mols for x being based on the observed water-transport over the concentration range 1-normal to 0·4-normal. These three values, when plotted against concentrations in equivalents per mol, lie also on a straight line which meets at infinite dilution the straight line representing the Hittorf transport number.

* *Wied. Ann.* 4, 503 (1878).

† *Loc. cit.*

‡ No data appear to be available for copper sulphate solutions of concentrations below 0·0212-normal.

The values of α for concentrations 0·327-normal to 0·0212-normal have been obtained on the assumption that x has a constant value of 1·63 over this concentration range and they agree fairly closely with the corresponding values read from the straight-line graph representing the true transport number. The values of the true transport number at 0·125-normal and lower concentrations appear to be little different from that (0·622) relating to infinite dilution as indicated by the point where the two straight-line graphs meet the axis.

§ 5. ACKNOWLEDGMENTS

The author desires to thank Prof. A. Griffiths for facilities provided and for the interest he has taken in this investigation.

The glass apparatus employed was made from the author's design by Messrs Gallenkamp.

DISCUSSION

Dr L. Simons. Does not the actual presence of the material of the diaphragm affect the concentration of the electrolyte in its immediate neighbourhood? This effect was dealt with by J. J. Thomson*. In view of Thomson's remarks it seems that very little meaning can be attached to the mean value of the concentration throughout the body of the solution. This would seem to have some very close relation to the apparent constancy of the liquid transport for high average concentrations as shown in table 1.

Dr V. Cofman. The author has explained that the observed flow across the diaphragm in dilute solutions is due to the combined effect of the electrolytic water-transport and the membrane effect caused by the Helmholtz double layer at the interface between parchment and solution (or within the capillaries of the membrane). How far does the curve calculated by the author for the Helmholtz effect† agree with that obtainable independently from cataphoretic measurements —i.e. from the rate of displacement, in an electric field, of small particles of parchment suspended in copper sulphate solution?

Author's reply. Adsorption of the electrolyte by the walls of the diaphragm would produce a change in concentration, but the equilibrium concentration in the diaphragm pores, after several washings with copper sulphate solution, appears to be little different from that in the body of the solution‡. It is pointed out also that the specific (electro-endosmotic) effect of the parchment diaphragm appears to be negligible in the case of copper sulphate solutions of 0·4-normal and higher concentrations.

A direct comparison between figure 3 and the results of cataphoretic measurements, as suggested by Dr Cofman, does not appear to be practicable owing to lack of experimental data relating to suspensions of parchment particles in copper sulphate solutions. The curve of figure 3 is of the same general character, however, as that met with in other cases of cataphoretic and allied electro-kinetic measurements.

---

* *Applications of Dynamics to Physics and Chemistry*, p. 190 (1888).

† Figure 3 (x, − 29·1).

‡ Cf. H. C. Hepburn, *Proc. Phys. Soc.* 38, 372 (1926).

THE SPECTRA OF TREBLY AND QUADRUPLY IONIZED ANTIMONY, Sb IV AND Sb V

By J. S. BADAMI, Imperial College, South Kensington

Read June 5, 1931

ABSTRACT. A study of the spark spectrum of antimony under varying conditions of excitation has led to an extension of the existing classification of the spectrum of Sb IV. Many new lines are classified as secondary members of the series. A second P term has been established for the Sb V spectrum.

§ 1. THE SPECTRUM OF Sb IV

An analysis of trebly-ionized antimony was given by Green and Lang* and partly independently by Gibbs and Vieweg† who also modified some conclusions of the former authors and extended their results. The investigations of Gibbs and Vieweg were, however, confined chiefly to the extreme ultra-violet region and extended only to λ 2113·14. The present communication is an extension of the investigation of the spectrum towards the region of longer wave-lengths. Many strong lines characteristic of the trebly-ionized atom have been found and have been classified as secondary members of the series system.

§ 2. EXPERIMENTAL

The spectrum of a condensed spark between poles of metallic antimony was studied under varying conditions of excitation, both in an atmosphere of air and in one of hydrogen. A large induction-coil running on 110 volts d.c. with mercury break was used. The spark in hydrogen easily brought out the lines of Sb IV. These appear relatively intense at tips with the spark in air, and fade away rapidly on diminution of the auxiliary spark gap in series and reduction of the capacity in parallel with the circuit. Plates were taken also with a one-meter vacuum-grating spectrograph, extending down to about λ 1280, a fluorite window being used, and the effect of inductance on the spark in a hydrogen atmosphere was studied. Kimura and Nakamura‡ and Soulillou§ have assigned some of the stronger lines of the spark spectrum to the various stages of ionization. Except for the line λ 2557·45, the lines used in the present investigation are in conformity with their assignments. λ 2557 has been assigned to Sb II by Soulillou and to Sb III by Kimura and Nakamura. Experiments show however that it certainly cannot belong to Sb II and may well belong to Sb IV. The lines given by the source are very diffuse and the weaker ones especially can be measured only with difficulty. For the stronger lines existing measurements by Soulillou have been utilized.

---

* *Proc. Nat. Acad. Sc.* **14**, 706 (1928).

† *Phys. Rev.* **34**, 400 (1929).

‡ *Jap. Journ. Phys.* **3**, 217 (1924).

§ *Comptes rendus*, **188**, 1103 (1929).

§ 3. PREDICTED TERMS

The term-scheme for the spectrum of Sb IV is presented in table 1. The term-prefix indicates the electronic configuration in a form convenient for writing. The notation used is that proposed by Russell, Shenstone and Turner[*]. The symbol ° denoting the odd terms is omitted as this is considered unnecessary when the configuration is given.

Table 1. Predicted terms of Sb IV.

Orbits of outer electrons													Term-prefix	Terms	
4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	7_1		Singlets	Triplets
2	6	10		2									$5s^2$	^1S	
2	6	10		1	1								$5s5p$	^1P	^3P
2	6	10		1		1							$5s5d$	^1D	^3D
2	6	10			2								$5p^2$	^1D ^1S	^3P
2	6	10		1					1				$5s6s$	^1S	^3S
2	6	10		1						1			$5s6p$	^1P	^3P
2	6	10	1	1									$5s4f$	^1F	^3F
2	6	10		1							1		$5s6d$	^1D	^3D
2	6	10		1								1	$5s7s$	^1S	^3S

§ 4. CATALOGUE OF NEWLY CLASSIFIED LINES OF Sb IV

A catalogue of newly classified lines of Sb IV is given in table 2. The first column gives the wave-lengths and intensities, wave-lengths to λ 2000 being in air and those smaller than λ 2000 *in vacuo*. The second column gives the wave-numbers *in vacuo* followed in the third column by the classification.

§ 5. IDENTIFICATION OF TERMS

Some difficulty was experienced in assigning the $5s6p\ ^3P_0$ level. Two possible choices for the $5s5d\ ^3D_1$–$5s6p\ ^3P_0$ transition were λ 2786·00 and λ 2857·07. Kimura and Nakamura[†] put λ 2786·00 in the list of Sb IV lines, but Soulillou[†] assigns it to Sb III and it has been classified by Lang[‡] as $5s^2 5d\ ^2D_{2\frac{1}{2}}$–$5s^2 5f\ ^2F_{2\frac{1}{2}}$. It may be noted that the similar transition is often very faint in spectra like Sb III. My experiments however indicate that the line more probably belongs to Sb III; no other satisfactory combination could be found with the $^3P_0$ level so obtained. λ 2857 being taken as the required transition, a fairly strong line at λ 2451·67 could be classified as $5s6p\ ^3P_0$–$5s5d\ ^3D_1$, but no combinations were obtained with the ^3S terms. Along with the two lines λ 3687·11 and λ 3425·89, classified as the $5s6s\ ^3S_1$ combinations with $5s6p\ ^3P_1$ and $^3P_2$, a remarkably similar line at λ 3735·26 led me to classify it as the $5s6s\ ^3S_1$–$5s6p\ ^3P_0$ transition, giving the $^3P_0$–$^3P_1$ difference identical with the $6s5d$ ($^3D_1$–$^3D_2$) difference, so that λ 2740·99 was classified doubly as $5s5d\ ^3D_2$–$5s6p\ ^3P_1$ and as $5s5d\ ^3D_1$–$5s6p\ ^3P_0$. This was further supported by the location of $5s6p\ {}^3P_0$–$5s7s\ {}^3S_1$ in the calculated position. The line $5s6p\ {}^3P_0$–$5s6d\ {}^3D_1$ was not found and is probably masked by λ 2543·82, a strong line of Sb II which is very near the calculated position.

---

[*] *Phys. Rev.* **33**, 900 (1929).

[†] *Loc. cit.*

[‡] *Phys. Rev.* **35**, 445 (1930).

Table 2. Newly classified lines of Sb IV.

λ air (Int.)	ν	Classification
3922·46 (1)	25487·0	$5s4f\ {}^1F_3$–$5s6d\ {}^3D_3$
3735·26 (5)	26764·3	$5s6s\ {}^3S_1$–$5s6p\ {}^3P_0$
*3687·01 (8)	27114·6	$5s6s\ {}^3S_1$–$5s6p\ {}^3P_1$
3618·99 (3)	27624·2	$5s4f\ {}^3F_2$–$5s6d\ {}^3D_1$
3611·49 (3)	27681·5	$5s4f\ {}^3F_3$–$5s6d\ {}^3D_2$
3599·37 (3)	27774·8	$5s4f\ {}^3F_4$–$5s6d\ {}^3D_3$
3578·8 (0)	27934	$5s4f\ {}^3F_3$–$5s6d\ {}^3D_3$
*3425·89 (10)	29181·2	$5s6s\ {}^3S_1$–$5s6p\ {}^3P_2$
*3287·70 (4)	30407·7	$5s6s\ {}^3S_1$–$5s6p\ {}^1P_1$
2803·79 (1)	35655·5	$5s6p\ {}^1P_1$–$5s6d\ {}^3D_1$
2792·7 (0)	35797	$5s6P\ {}^1P_1$–$5s6d\ {}^3D_2$
*2740·99 (10)	36472·4	$5s5d\ {}^3D_1$–$5s6p\ {}^3P_0$
†2740·99 (10)	36472·4	$5s5d\ {}^3D_2$–$5s6p\ {}^3P_1$
*2714·96 (5)	36822·1	$5s5d\ {}^3D_1$–$5s6p\ {}^3P_1$
2710·7 (00)	36880	$5s6p\ {}^3P_2$–$5s6d\ {}^3D_1$
*2700·11 (5)	37024·6	$5s6p\ {}^3P_2$–$5s6d\ {}^3D_2$
*2681·77 (6)	37277·7	$5s6p\ {}^3P_2$–$5s6d\ {}^3D_3$
*2632·10 (10)	37981·2	$5s5d\ {}^3D_3$–$5s6p\ {}^3P_2$
*2594·10 (6)	38537·5	$5s5d\ {}^3D_2$–$5s6p\ {}^3P_2$
2570·9 (0)	38885	$5s5d\ {}^3D_1$–$5s6p\ {}^3P_2$
2566·92 (2)	38945·5	$5s6p\ {}^3P_1$–$5s6d\ {}^3D_1$
*2557·45 (4)	39089·7	$5s6p\ {}^3P_1$–$5s6d\ {}^3D_2$
*2514·08 (4)	39764·0	$5s5d\ {}^3D_2$–$5s6p\ {}^1P_1$
2501·19 (4)	39968·9	$5s6p\ {}^3P_2$–$5s7s\ {}^3S_1$
2492·15 (1)	40113·9	$5s5d\ {}^3D_1$–$5s6p\ {}^1P_1$
2378·32 (2)	42033·6	$5s6p\ {}^3P_1$–$5s7s\ {}^3S_1$
2358·6 (1)	42385	$5s6p\ {}^3P_0$–$5s7s\ {}^3S_1$
2278·03 (4)	43884·0	$5s6p\ {}^1P_1$–$5s7s\ {}^1S_0$
2116·1 (0)	47242	$5s5d\ {}^3D_3$–$5s4f\ {}^3F_2$
λ vac.		
1915·39 (2)	52209	$5p^2\ {}^3P_2$–$5s6p\ {}^3P_1$
1801·79 (6)	55500	$5p^2\ {}^3P_2$–$5s6p\ {}^1P_1$
1585·17 (2)?	63085	$5s5d\ {}^1D_2$–$5s6p\ {}^1P_1$
1406·59 (1)	71094	$5s5d\ {}^1D_2$–$5s4f\ {}^3F_2$
1358·13 (5)	73631	$5s5d\ {}^1D_2$–$5s4f\ {}^1F_3$

* λ by Soullillou. † Used twice.

It is interesting to compare the ratio $({}^3P_1$–${}^3P_2) : ({}^3P_0$–${}^3P_1)$ for the $5s6p$ configuration in the iso-electronic spectra as is done in table 3. It is evident from the last column that with the increase of nuclear charge there is a gradual deviation from the Russell-Saunders coupling which leads to the theoretical ratio 2 : 1. If we classify λ 2857 as the $5s5d\ {}^3D_1$–$5s6p\ {}^3P_0$ transition the ratio in question becomes 2066 : 1832 = 1·12. Comparison of this with the ratios for other iso-electronic spectra further justifies us in rejecting λ 2857·07 and using λ 2740·99 twice.

The $5s5d\ {}^1D_2$ and $5p^2\ {}^1D_2$ levels as given by previous authors are interchanged, as it is thought that the $5s5d\ {}^1D_2$–$5s5p\ {}^3P$, ${}^1P$ combinations would be more likely than the $5p^2\,{}^1D_2$–$5s5p\,{}^3P$, ${}^1P$ combinations. The conclusion that the $5s5d\,{}^1D_2$ level then becomes deeper than the $5s5d\,{}^3D$ levels is justified from comparison with the Cd I spectrum, where both $5s5d\,{}^1D_2$ and $5s6d\,{}^1D_2$ are deeper than the respective ${}^3D$ terms. In In II also the $5s5d\,{}^3D$, ${}^1D$–$5s4f\,{}^3F$, ${}^1F$ combinations as given by McLennan and Allin* show that the ${}^1D_2$ is much deeper than the ${}^3D$ terms of the same $5s5d$ configuration. A similar change may be suggested for the Sn III spectrum.

Table 3. $5s6p$ (${}^3P_1$–${}^3P_2$) : (${}^3P_0$–${}^3P_1$).

Element	${}^3P_1$–${}^3P_2$	${}^3P_0$–${}^3P_1$	Ratio
Cd I	174	71	2·45
In II	558	182	3·07
Sn III	1223	273	4·48
Sb IV	2066	350	5·90

λ 2278·03, given as the $5s6p\,{}^1P_1$–$5s7s\,{}^1S_0$ combination of Sb IV, seems to be the most suitable line in the probable region.

A strong line, λ 1584·59, appears to be double, with a fainter component at λ 1585·17. The strong line itself does not seem to be characteristic of Sb IV, and the fainter one being near the calculated position of $5s5d\,{}^1D_2$–$5s6p\,{}^1P_1$, the transition is classified as such.

The spectrum of Sb IV is given in multiplet form† in table 4, previous results of Green and Lang and of Gibbs and Vieweg being also included for the sake of completeness. The term-values for the deepest terms, as calculated from the available series by Gibbs and Vieweg, are used, the others being calculated from the observed frequencies.

§ 6. THE SPECTRUM OF Sb V

While plates taken with an antimony spark in hydrogen with a Hilger E. 1 quartz spectrograph were being examined, two lines, λλ 3362·94 and 3036·16, which were intense and yet appeared as distinct from other lines only at the tips, were observed. No trace of these lines was found on plates taken with the spark in air.

---

* *Proc. R.S.* A, **129**, 208 (1930).

† In agreement with the known term-values of the Sn III spectrum (Gibbs and Vieweg, *loc. cit.*), the following $5s6p\,{}^3P$, ${}^1P$–$5s6d\,{}^3D$, ${}^1D$ combinations in Sn III have been identified. The wave-lengths are taken from Kayser's *Handbuch*, Band VI, and corrected to I.A. The lines are classed as due to Sn III by Kimura and Nakamura (*loc. cit.*).

	$5s6p\,{}^3P_0$	274	${}^3P_1$	1222	${}^3P_2$	${}^1P_1$
$5s6d\,{}^3D_1$	27974 3573·7 (1*u*)		27700 3609·1 (–)			
78						
${}^3D_2$			27778 3598·9 (2*u*)		26556 3764·5 (1*u*)	
134						
${}^3D_3$					26690 3745·6 (2*r*)	
,, ${}^1D_2$						26961 3708·0 (2*u*)

Table 4. Combinations in Sb IV.

Terms	$5s5p\,{}^3P_0$ 291721	${}^3P_1$ 289456	${}^3P_2$ 283596	${}^1P_1$ 260204	$5s6p\,{}^3P_0$ 140770	${}^3P_1$ 140420	${}^3P_2$ 138354	${}^1P_1$ 137128	$5s4f\,{}^3F_2$ 129097	${}^3F_3$ 129012	${}^3F_4$ 128852	${}^1F_3$ 126564
$\Delta\nu$		2265	5860	23392		350	2066	1226		85	160	2288
$5s^2\,{}^1S_0$ 356156		66700 1499·24 (25)		95950 1042·21 (75)		215763 463·47 (0)		219058 456·50 (1)				
$5s6s\,{}^3S_1$ 167534	124187 805·24 (15)	121920 820·21 (25)	116063 861·60 (25)		26764·3 3735·26 (5)	27114·6 3687·01 (8)	29181·2 3425·89 (10)	30407·7 3287·70 (4)				
$5s7s\,{}^3S_1$ 98385	193334 517·24 (00)	191064 523·38 (3)	185219 539·90 (6)		42385 2358·6 (1)	42033·6 2378·32 (2)	39968·9 2501·19 (4)					
5141 ${}^1S_0$ 93244								43884·0 2278·03 (4)				
$5s5d\,{}^3D_1$ 177242	114474 873·56 (20)	112212 891·17 (20)	106351 940·28 (6)	82975 1205·18 (15)?	*36472·4 2740·99 (10)	36822·1 2714·96 (5)	38885 2570·9 (0)	40113·9 2492·15 (1)	48146 2076·33 (5)			
350 ${}^3D_2$ 176892		112562 888·40 (25)	106704 937·17 (15)	83311 1200·32 (00)		*36472·4 2740·99 (10)	38537·5 2594·10 (6)	39764·0 2514·08 (4)	47795 2091·59 (2)	47880 2087·86 (10)		
556 ${}^3D_3$ 176336			107259 932·32 (25)				37981·2 2632·10 (10)		47242 2116·1 (0)	47323 2112·47 (3)	47483 2105·33	
−23864 ${}^1D_2$ 200200		89255 1120·38 (8)	83396 1199·10 (25)	59991 1666·93 (15)				†63085 1585·17 (2)?	71094 1406·59 (1)			73631 1358·13 (5)
$5s6d\,{}^3D_1$ 101473		187956 532·04 (00)			[39297 2543·96] §	38945·5 2566·92 (2)	36880 2710·7 (00)	35655·5 2803·79 (1)	27624·2 3618·99 (3)			
143 ${}^3D_2$ 101330		188132 531·54 (1)	182255 548·68 (0)			39089·7 2557·45 (4)	37024·6 2700·11 (5)	35797 2792·7 (0)		27681·5 3611·49 (3)		
253 ${}^3D_3$ 101077			182515 547·90 (4)				37277·7 2681·77 (6)			27934 3578·8 (0)	27774·8 3599·37 (3)	25487·0 3922·46 (1)
479 ${}^1D_2$ 100598				159606 626·54 (2)								
$5p^2\,{}^3P_0$ 204080		85370 1171·38 (20)										
4312 ${}^3P_1$ 199768	91942 1087·64 (8)	89682 1115·05 (25)	83828 1192·92 (25)	60426 1654·93 (00)								
7136 ${}^3P_2$ 192632		96817 1032·88 (30)	90964 1099·33 (30)	67565 1480·05 (15)?		52209 1915·39 (2)		55500 1801·79 (6)				
19277 ${}^1D_2$ 173355				86844 1151·49 (40)?								

* Used twice.

† Hardly resolved from a strong diffuse line λ 1584·6 of lower stage of ionization.

§ Probably masked by a strong line λ 2543·82 of Sb II.

They are attributed to Sb V and are classified as the first doublet of the second principal series. The irregular doublet law applied to the particular transitions in Ag-I-like isoelectronic spectra* justifies this classification beyond doubt, as the following table 5 shows.

Table 5. $6\ {}^2S_{\frac{1}{2}}$–$6\ {}^2P_{\frac{1}{2},\,1\frac{1}{2}}$ transitions in Ag-I-like spectra.

Element	$6\ {}^2S_{\frac{1}{2}}$–$6\ {}^2P_{\frac{1}{2}}$			$6\ {}^2S_{\frac{1}{2}}$–$6\ {}^2P_{1\frac{1}{2}}$		
	ν	$\Delta\nu$	$\Delta^2\nu$	ν	$\Delta\nu$	$\Delta^2\nu$
Ag I	(5741)†			(5946)†		
		5978			6447	
Cd II	11719		14	12393		208
		5992			6655	
In III	17711		11	19048		188
		6003			6843	
Sn IV	23714		10	25891		193
		6013			7036	
Sb V	29727			32927		

By application of Sommerfeld's fourth power law $\Delta\nu = K(Z-s)^4$ to the $6\ {}^2P_{\frac{1}{2}}$–$6\ {}^2P_{1\frac{1}{2}}$ separation, the values of the screening constant s calculated for Ag-I-like spectra are compared in table 6.

Table 6. Screening constants for $6\ {}^2P_{\frac{1}{2}}$–$6\ {}^2P_{1\frac{1}{2}}$ separations in Ag-I-like spectra.

Z	Element	$\Delta\nu$	$Z-s$ or $\sqrt[4]{(\Delta\nu/0{\cdot}0135)}$	s	Δs
47	Ag I	202·9	11·08	35·82	
					2·76
48	Cd II	672·8	14·94	33·06	
					1·80
49	In III	1337·4	17·74	31·26	
					1·30
50	Sn IV	2177·4	20·04	29·96	
					1·02
51	Sb V	3199·4	22·06	28·94	

Lang‡ has classified some lines in the extreme ultra-violet. Of these, λ 891·41, classified as $5\ {}^2P_{1\frac{1}{2}}$–$5\ {}^2D_{2\frac{1}{2}}$, has been shown to belong to Sb IV by Gibbs and Vieweg§ and they have suggested λ 888·97 instead. The suggestion seems to be justified by the location of the $5\ {}^2D$–$5\ {}^2P$ combination in the calculated position. The actual frequency calculated differs from that observed by an amount which may be accounted for by an error of about 0·3 Å.U. in the wave-length measure of the $5\ {}^2P$–$6\ {}^2S$ combinations. Table 7 shows the variation in the separations of $5\ D$

---

* The values for Ag I, Cd II, In III, and Sn IV are taken from a paper on the spectrum of Sn IV by K. R. Rao, *Proc. Phys. Soc.* **29**, 468 (1927).

† Calculated from known terms.

‡ *Proc. Nat. Acad. Sc.* **13**, 343 (1927).

§ *Loc. cit.*

terms in Ag-I-like spectra along with the screening constants. As will be seen from the table, the abnormal rise in the value of s for Sn IV is not continued for Sb V, and again for Te VI there is a normal decrease.

Table 7. Screening constants for $5\,^2D_{1\frac{1}{2}}$–$5\,^2D_{2\frac{1}{2}}$ separations for Ag-I-like spectra.

Z	Element	$\Delta\nu$	$Z-s$ or $\sqrt[4]{(\Delta\nu/0\cdot00776)}$	s	Δs
47	Ag I	20·3	7·15	39·85	
					3·71
48	Cd II	154	11·86	36·14	
					0·95
49	In III	283	13·81	35·19	
					− 3·98
50	Sn IV	107	10·83	39·17	
					7·64
51	Sb V	1116	19·47	31·53	
					0·97
52	Te VI*	1644	21·44	30·56	

Lang classified λ 1505·70 and λ 1524·47 as the $5\,^2D_{1\frac{1}{2},\,2\frac{1}{2}}$–$5\,^2F$ transitions. These lines appear to be due to lower stages of ionization, probably Sb II or III.

As for Sb IV, the results as known to-day are shown in a multiplet form in table 8. The term-value 449300 for $5\,^2S$ given by Lang is retained.

Table 8. Combinations in Sb V.

Terms $\Delta\nu$	$5\,^2P_{\frac{1}{2}}$ 367734	$5\,^2P_{1\frac{1}{2}}$ 358747	$6\,^2P_{\frac{1}{2}}$ 194920	$6\,^2P_{1\frac{1}{2}}$ 191721
	8987		*3199*	
$5\,^2S_{\frac{1}{2}}$ 449300	†81566 1226·00 (12)	†90553 1104·32 (8)	—	—
$5^2\,D_{1\frac{1}{2}}$ 247373	120337 831·00 (6)	†111356 898·02 (1)	52453 1906·47 (7)	‡55652 1796·89 (5)
1116				
$5^2\,D_{2\frac{1}{2}}$ 246257		§112490 888·97		54536 1833·65 (8)
$6^2\,S_{\frac{1}{2}}$ 224647	†143017 699·22 (3)	†134037 746·06 (1)	29727·4 3362·94 (8)	32926·8 3036·16 (10)

§7. ACKNOWLEDGMENTS

In conclusion the author takes this opportunity of expressing his thanks to Prof. A. Fowler, F.R.S., for his interest and encouragement throughout the course of this investigation. His thanks are also due to the University of Bombay for the award of a Scholarship.

---

* The author's thanks are due to Dr K. R. Rao for supplying the data for Te VI prior to publication.

† $\lambda\lambda$ and classification by Lang.

‡ This line may also belong to Sb II or III.

§ Suggested by Gibbs and Vieweg.

THE HIGH-FREQUENCY SPECTRUM OF MERCURY AND THE FINE STRUCTURES OF λ 6123 (Hg I) AND λ 4797 (Hg II)

By S. TOLANSKY, B.Sc., Armstrong College,
Newcastle-upon-Tyne, Durham University

Communicated by G. W. Todd, M.A., D.Sc., *April* 30, 1931.

ABSTRACT. It is shown that the previously reported intensity-modifications, found to take place in the high-frequency electrodeless discharge in mercury vapour at low pressures (0·001 mm.), can be completely explained in terms of recently determined electron-impact excitation curves. The modified spectrum arises from the fact that the mean free path is large, enabling the electrons to attain high velocities which result in the strengthening of lines involving upper singlet levels. The high-frequency spectrum at a pressure of 3 mm. is found to be arc-like, supporting the above conclusion.

The fine structure of the unclassified line λ 6123 (Hg I) is determined with a Fabry-Perot interferometer and found to have eight components. Four of these form a multiplet and may arise from one isotope only. The line λ 6123 probably involves an upper singlet level. The unclassified spark line λ 4797 (Hg II) shows four fine-structure components, widely separated and of similar intensities.

§ 1. INTRODUCTION

A description of the spectrum of mercury vapour excited at very low pressures by a high-frequency electrodeless discharge has already been given[*]. The discharge was produced in pure mercury vapour at room temperature, contained in a pyrex tube 10 cm. long and 2 cm. in bore, having a central capillary portion 1 cm. long and 0·25 cm. in bore. Strips of tinfoil were wrapped round the wider parts and these were coupled inductively to a lecher-wire system in which oscillations of a wave-length of about 7 metres were maintained by a valve (a Mullard D.O. 40 operated with a 6-volt filament battery and 480-volts high-tension[†].

The triplet line λ 3341 being taken as the basis of comparison, many other lines show a marked change of intensity in the high-frequency discharge as compared with the arc[‡]. The intensity-modifications may be summarized in the statements that all allocated lines involving singlet levels as upper states are considerably strengthened whether they be singlet or intercombination lines, whilst intercombination lines involving upper triplet levels are somewhat weakened. In all the observed series, including triplets, the higher series-members are relatively stronger than in the arc, but this effect is not very marked. The unclassified lines show three types of behaviour, namely marked strengthening, marked weakening and very slight indication of change. Since strengthening in all allocated lines is invariably associated with upper singlet levels, it was suggested that the strengthened unclassified lines involve upper singlet levels. It is also to be expected that the weakened unclassified lines involve upper triplet levels and that those which are unchanged may arise from displaced triplet terms. The lines λ 5461 and λ 4047, which involve metastable levels, are very heavily absorbed. The degree of intensity-modification is found to be reduced when the current density through the tube is increased.

---

[*] *Proc. Phys. Soc.* **42**, 556 (1930).

[†] S. F. Evans, *J. Sci. Inst.* **7**, 261 (1930).

[‡] The line λ 3341 is the second number of the series to which λ 5461 belongs and is used because the latter is very strongly absorbed in the high-frequency discharge.

In the first part of this paper an attempt is made to account for these intensity-modifications, and in the second part the fine structures of two of the enhanced lines are discussed.

§ 2. EXPERIMENTAL

It was found that a very great increase in both the relative and the absolute intensities of the enhanced* lines took place if the capillary tube was replaced by a tube 20 cm. long and 3 cm. in bore. In order to obtain the maximum illumination possible, a tube 150 cm. long and 3 cm. in bore was finally employed, and when viewed end on this gave a brilliant enhanced spectrum. Part of the spectrum obtained is shown at (*a*) in the plate. For this particular photograph a 250-watt oscillator (wave-length 20 metres)† was used. The tube remained cold when running, the vapour-pressure of the mercury being of the order of 0·001 mm. The spectrum was photographed with the Hilger constant-deviation instrument on Ilford soft-gradation panchromatic plates developed in hydroquinone. In the plate (*b*) is the spectrum of an ordinary vacuum mercury arc carrying 2 amp. The enhancements are very striking.

A small capillary tube as previously employed was placed in a furnace and showed the enhanced spectrum in the cold. As the temperature was raised the singlets weakened and the triplets strengthened until at 150° C. the discharge was practically identical with that of the arc; see (*c*) in the plate.

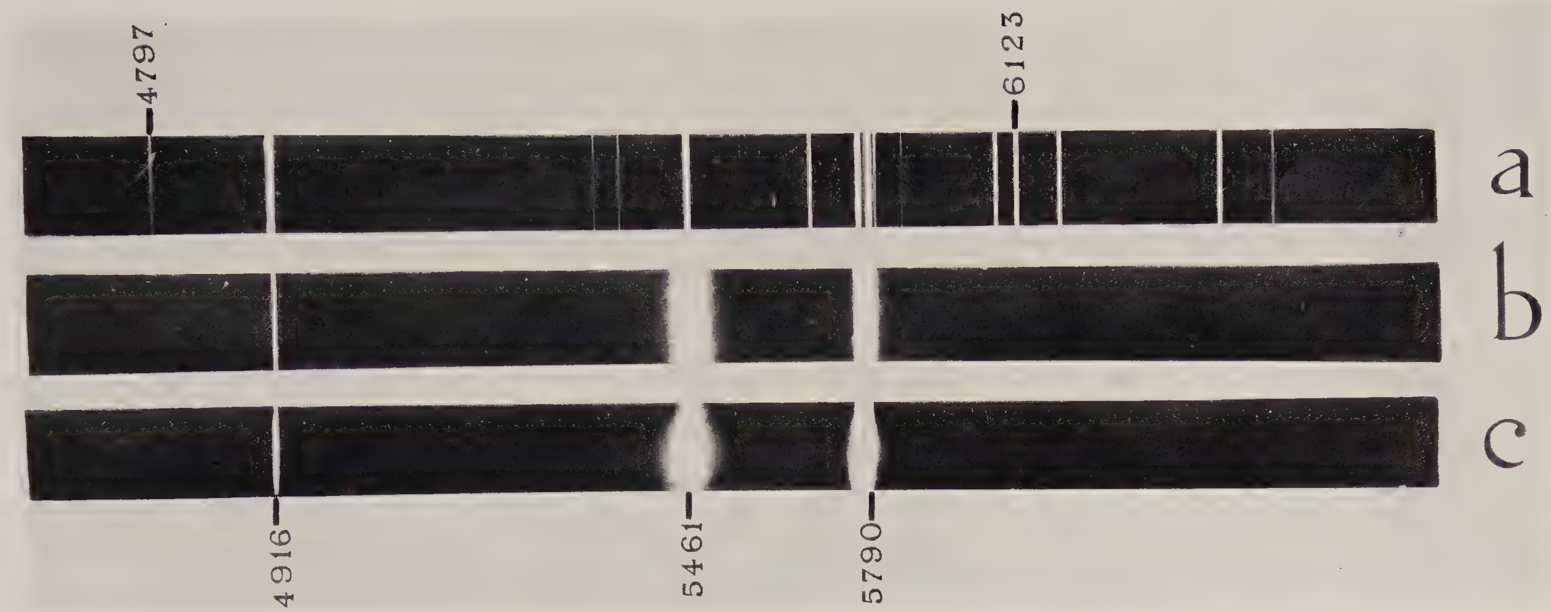
This behaviour of the high-frequency discharge in mercury vapour at different pressures is explained by a recent investigation of Schaffernicht‡ on the excitation of the mercury spectrum by electron impact. Working at low pressures (0·001 mm.), Schaffernicht bombarded mercury vapour with electrons of varying velocity. He found that every line of the spectrum showed an optimum electron voltage, for which the line was emitted with maximum intensity. Voltage intensity curves were plotted, and it was found that the form of each curve was entirely dependent upon the upper level involved. In general, lines of the same series had very similar

---

* The term "enhanced" when employed in this paper is meant to indicate strengthening in the high-frequency discharge relative to the arc, and has no reference to spark lines.

† R. L. Smith-Rose and J. S. Mc. Petrie, *Exp. Wireless*, **6**, 532 (1929).

‡ *Zeit. für Phys.* **62**, 106 (1930).



High frequency discharge in mercury vapour: (*a*) pressure 0·001 mm., (*b*) mercury arc, (*c*) pressure 3 mm.

Fabry-Perot fringes of unclassified arc line λ6123. Plate separation = 6·5 mm. Separation of orders = 0·286 A.U.

excitation curves. There were two main types of curve, singlet type and triplet type, and these are shown in figure 1, which is taken from Schaffernicht. Lines with upper singlet term, as a rule, show a flat maximum at about 30 volts, whilst lines with upper triplet term show a very steep maximum at about 11 volts. Only two exceptions occur, namely lines involving $^1S_0$ and $^3D_2$ as upper levels. These have two maxima of singlet and triplet types, the curves however tending rapidly to become normal for terms of higher principal quantum number n. According to Schaffernicht, the exceptions are due to excitation of terms partly by direct impact and partly by stepwise transitions from previously excited triplet terms in the case of the $^1S_0$ levels, and singlet terms in the case of the $^3D_2$ levels. With very high voltages both singlet- and triplet-type curves become flat.

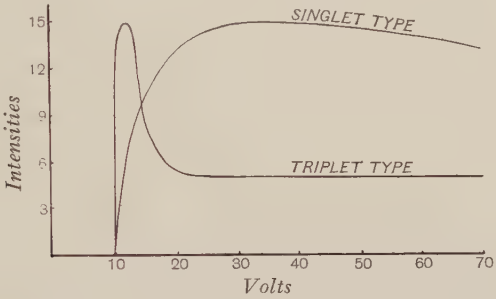


Fig. 1. Electron-impact excitation curves in mercury (after Schaffernicht)

It is at once apparent from the curves that in changing from low- to high-voltage excitation there is a very marked relative strengthening of the lines involving upper singlet terms. The spectrum produced with low-voltage electrons is identical with that of the arc (and high-frequency discharge at 150° C.), whilst that formed by high-voltage electrons is similar to that given by the high-frequency discharge at room temperature. It is reasonable to conclude that in the arc and high-temperature high-frequency discharge the effective electron voltage is small, whilst in the case of the cold discharge it is high. Consideration of the mean free paths shows that this is very probably the explanation of the enhanced spectrum. In the long tube at room temperature the mean free path of mercury atoms is about 7 cm. The electrons produced by the discharge have therefore sufficient time to acquire a high velocity before striking mercury atoms. The electrons are then effectively high-voltage electrons, the result being a spectrum in which lines with singlet-type excitation curves are markedly strengthened. When the temperature of the tube is raised to 150° C. the pressure of mercury vapour is about 3 mm. and the mean free path is of the order of only 0·003 cm. With such a short mean free path the probability of electrons acquiring a high velocity is small, so that their effective voltage is low. Since this low-voltage excitation condition also exists in the arc, the discharge reverts to arc type, wherein the triplets are much stronger than singlets; see (*c*) in the plate. There should be an optimum pressure, depending on the power used and on its frequency, which will give a maximum enhancement of the singlets.

The increase in intensity of the singlet-type lines on changing over from the capillary tube to the wider and longer tube is further evidence that the mean free path determines the degree of enhancement. It is very probable that the restricted dimensions of the capillary tube were such as to prevent electrons from attaining their full velocity, i.e. they were equivalent to a reduction in mean free path. The influence of mean free path on the type of spectrum produced by the high-frequency discharge is shown in a different manner by the discharge in iodine vapour. A tube containing iodine at room temperature shows the arc spectrum. If a side limb is cooled with ice the pressure is reduced and the arc lines diminish rapidly in intensity, strong spark lines appearing instead. With the reduction in pressure the mean free path increases and with it the effective electron voltage. As a result of the more intensive bombardment strong ionization occurs and practically none but spark lines appear. Pressure-control, then, affords a convenient means of producing either the arc or the spark spectrum. It is found that bromine behaves in an exactly similar way*.

§ 3. FINE STRUCTURE OF λ 6123

The arc line λ 6123 has not yet been classified. It is very strongly enhanced in the high-frequency discharge and, since both temperature and pressure are low, very sharp lines result. This line was photographed along with the singlets previously examined†, but analysis was deferred since a great deal of trouble was experienced from overlapping orders. While the author was engaged upon the work a communication was received from Venkatesachar and Sibaiya‡ giving the structure of this line. Their results are not in agreement with those obtained here and will be discussed later.

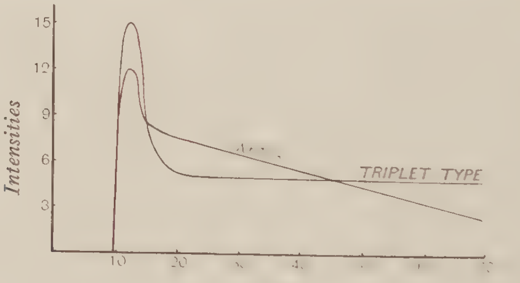


Fig. 2. Excitation curves of triplet-type lines and of λ 6123 (after Schaffernicht).

The fine structure was determined with a silvered Fabry-Perot interferometer (Hilger N. 71) having a plate-separation continuously variable from 2·6 to 100 mm. The plates are of quartz and have an aperture of 6 cm. The interferometer was crossed with a Hilger large quartz E. 1 spectrograph, and exposures varied from one to seven hours. The spectrograms were taken on Ilford soft-gradation panchromatic plates developed in hydroquinone. The tube employed was 150 cm. long, and a 7-metre oscillator was used to produce the discharge. Since the fine structure extends over a width of 0·395 Å.U., overlapping of adjacent orders takes place even for small gaps such as 5 mm. A completely unambiguous determination of the structure was only obtained by the use of gaps increasing steadily by half-millimetres from 4 to 9 mm. The fringes reproduced in the plate were obtained with a 6·5 mm. gap and 2 hours' exposure. The weaker components do not appear in the reproduction, and the closer components are completely resolved with higher plate-separations. There are eight components and these with their estimated intensities are shown in figure 3.

---

* Unpublished data of S. F. Evans.

† *Proc. R.S.* A, **130**, 558 (1931).

‡ *J. Mysore Univ.* **5**, **145** (1930).

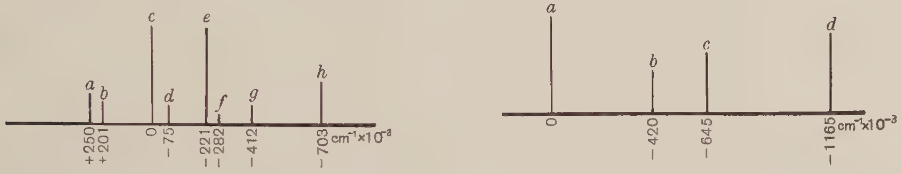


Fig. 3. Fine structure of λ 6123 of Hg I (left-hand curve) and λ 4797 of Hg II (right-hand curve).

Table 1 gives the observed structure together with that found by Venkatesachar and Sibaiya. The structures are given in thousandths of a wave-number. The extreme limits of error are indicated but the probable error is certainly less, since the values are the means of several determinations, mostly close together.

Table 1. Fine structure of λ 6123 (Hg I).

Venkatesachar and Sibaiya		Author		
		+ 250 ± 3	(3)	*a*
+ 171	(5)	+ 201 ± 2	(2)	*b*
0	(10)	0	(10)	*c*
− 117	(3)	− 75 ± 3	(2)	*d*
− 221	(8)	− 221 ± 1	(10)	*e*
− 323	(1)	− 282 ± 4	(1)	*f*
		− 412 ± 2	(2)	*g*
		− 703 ± 4	(4)	*h*

A comparison of the two structures shows that there is exact agreement in the case of the strong lines *c*, *e*, but none in the case of other lines. In considering the discrepancy a number of factors must be taken into account, since both the sources and interferometers used differed in the two cases. The Fabry-Perot interferometer used in the present work is of course free from ghost images, and with it difficulties due to overlapping may be completely resolved. The fringes are extremely narrow in the high-frequency discharge and there is no evidence of reversal since the structure is not dependent on the depth of vapour penetrated, and very sharp fringes are still obtained with big plate-separations such as 6 cm. Venkatesachar and Sibaiya used Lummer plates and an echelon, the source being a low-current branched arc. As has been shown, the intrinsic intensity of enhanced lines is very much greater in the high-frequency discharge than in the arc, and this explains why these investigators observed fewer components. It is noteworthy that exact agreement is obtained with the strongest pair only, a result which is to be expected if one source is weak. The other lines given by Venkatesachar and Sibaiya are either ghosts or, more probably, misinterpretations due to the excessive overlapping. This would cause serious trouble with any interferometer not continuously variable. A further possibility is that the structures actually differ in the two discharges, but this is not very likely, as has previously been shown.

An attempt to fit the components of λ 6123 into a term scheme has met with partial success. The four components *e*, *h*, *b*, *f* can be arranged in square form, and give two pairs of equal differences. This result is shown in table 2. If it is not spurious, it means that the four lines are the four transitions obtainable from two upper and two lower levels, the level-separation in one case being 422 and in the other 482. This is shown in figure 4, where the bigger separation has provisionally been allotted to the lower level.

Table 2.

− 282	(*483*)	+ 201
(*421*)		(*422*)
− 703	(*482*)	− 221

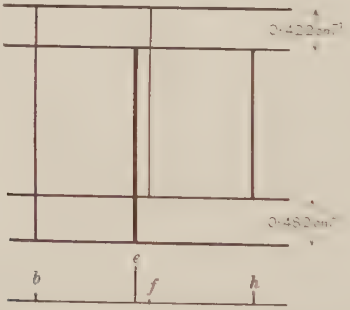


Fig. 4. Fine-structure multiplet in λ 6123.

It has previously been shown that the fine structures of singlet lines suggest that in mercury the two odd isotopes 199, 201 have different nuclear spins, each resulting in a characteristic fine structure, while the even isotopes have no nuclear spin and give single lines. If this is correct, then the above-mentioned quartet may arise from one isotope. Of the remaining four lines the strongest would belong to the even isotopes and the other three to the second odd isotope. The main difficulty of this viewpoint is the same as that experienced in considering the ringlets, namely, that since the abundance-ratios of even to odd isotopes, the even being summed, are about 5·1 : 1·2 : 1, only one very strong component would be expected, whereas two are observed.

It is well to point out that a spurious quartet can easily arise. Suppose three lines are distributed at random: if a fourth is accidentally placed so that a pair of equal differences results, then another pair of equal differences automatically exists. Hence the existence of the quartet can depend on the accidental situation of one line only. However, the differences in this case are very exact, agreeing to a thousandth of a wave-number, and they are therefore probably genuine.

§ 4. ALLOCATION OF λ 6123

Since this line is strongly enhanced in the high-frequency discharge, it is probable that it involves an upper singlet level. Schaffernicht has determined its excitation-function. This is shown in figure 2, a triplet-type curve also being plotted for comparison. Since the curve for λ 6123 shows a steep maximum at about 12 volts, Schaffernicht concludes that the line involves an upper triplet level. However, attention may be drawn to two facts: (*a*) The curve is distinctly different from the ordinary triplet-type curves. All lines involving upper triplet levels (other than the abnormal terms) have a steep maximum near 11 or 12 volts and then become practically flat and horizontal at about 20 volts. The curve for λ 6123 shows a steep maximum at 12 volts and then falls off steeply, showing no tendency to flatten even up to 70 volts. (*b*) If the line has an upper triplet level it should be stronger in the arc, but it is not.

A distinct possibility is that the mode of production of this line is different according as high-frequency excitation or electron-impact excitation is employed. This possibility may be connected with the difficulty hitherto experienced in classifying the line. Hanle* has found that the singlet and triplet excitation curves in helium are of a similar nature to those in mercury, showing the same types of maxima. However the singlet *He* line $2P - 4S$ (λ 5048) shows a curve not very different from λ 6123 in mercury, so that the curve itself does not give decisive evidence.

The fine structure of the line shows that a $^1S_0$ level cannot be involved in its production. It has been previously shown† that $7^1S_0 - 9^1P_1$ has seven components, and reasons were given why this should be the maximum number of components of a line involving a $^1S_0$ level. λ 6123 has been shown to possess eight components. A further point is that a $^1S_0$ level must always remain single for any given isotope, no matter what the value of the nuclear spin. If the quartet structure given in figure 4 is due to one isotope, then a $^1S_0$ level cannot be involved. If this quartet structure comprises the total structure for one of the isotopes, then the nuclear spin for this isotope must be $\frac{1}{2}$. However if one of the levels were triple and the other double the multiplet could have five components and there is no way of detecting whether or not one of the remaining lines is a fifth member, since j-values are unknown and no common differences involving the fifth line occur.

* *Zeit. für Phys.* **56**, 94 (1929).

† *Proc. R.S. loc. cit.*

§ 5. FINE STRUCTURE OF λ 4797 (Hg II)

Very little attention has been given to the fine structures of the lines of ionized mercury. Schüler* mentions intensity-measurements in the Hg II lines λ 7944 and λ 6150 but gives no details as to structure. Venkatesachar and Sibaiya† state that λ 3984, which is $^2D_{\frac{5}{2}} - 2^2P_{\frac{3}{2}}$ according to Paschen, has six components, but they give no details. The writer has been unable to find any other reference to the fine structure of Hg II. Naudé‡ gives the line λ 4797 as by far the strongest line of the Hg II spectrum and it has not yet been classified. Paschen§ found many stronger lines in the spectrum, but he employed a discharge-tube with mercury in helium, and Naudé has shown that helium modifies the intensity-distribution. The line can be brought up in the high-frequency discharge if the discharge is sufficiently intense: (*a*) in the plate. Since two high-frequency oscillators were available, one of 250 watts with wave-length 20 metres and the other of 40 watts with wave-length 7 metres, both were coupled to the tube simultaneously. This resulted in a marked brightening of the line, and as the pressure and temperature were still low the line was not broadened. It was photographed with the Fabry-Perot interferometer on Ilford Monarch plates developed in hydroquinone, exposures up to two hours being sufficient. Since fine-structure separations increase with the degree of ionization, the structure is therefore much coarser than that appearing in the mercury arc lines. This resulted in frequent overlapping of orders, so that plate-separations of from 2·65 to 8 mm. only could be employed. The resolving power in this region being much smaller than in the red, the accuracy of the measurements is lower than for λ 6123. The separations are given in thousandths of a wave-number and are likely to be accurate to within 5 units. Four components have been observed, but there may be closer unresolved members. It has been impossible to determine this with certainty, but an exposure with a 17·5 mm. plate-separation still showed four components only. The structure is given in table 3 and figure 2. Component *a* appears diffuse and may be complex.

Table 3. Structure of λ 4797 (Hg II).

0	(5)	*a*
− 420	(2)	*b*
− 645	(3)	*c*
− 1165	(4)	*d*

The structure is so coarse, the nearest components being 225 units apart, that it could be resolved on a good grating. It is hoped to make an attempt to examine the mercury spark lines with a 21-ft. grating. Schüler has pointed out that in a number of mercury lines the weaker components B_n group themselves about a very strong component A, so that the optical centre of gravity of ΣB_n coincides with A. He has examined the intensity-distribution in the arc lines λλ 4047, 4078, 4916, 5461, 5769, 5791 and in the spark lines λλ 6150, 7944, and in most of these he finds that the ratio $\Sigma B_n/G$ is between 25 and 32 per cent. where G is the total intensity of all the components. Since the odd isotopes form about 30 per cent. he suggests that the weaker fine-structure lines come from the odd isotopes. However, the arc lines λλ 5461, 2536 and the spark line λ 6150 do not give this ratio at all. It is at once apparent that λ 4797 also constitutes an exception, there being no single strong component, the structure is in fact somewhat similar in nature to that of the resonance line λ 2536* as regards intensity-distribution.

---

* *Naturwiss.* **43**, 895 (1930).

† *Loc. cit.*

‡ *Ann. d. Phys.* **3**, 1 (1929).

§ *Sitz. Preuss. Akad. Wiss.* **32**, 536 (1928).

It may be pointed out, with reference to Schüler's results, that the intensity-distribution in mercury-fine structures is partly dependent upon the mode of excitation and the degree of self-absorption.

§ 6. ACKNOWLEDGMENT

I wish to express my thanks to Prof. W. E. Curtis, who has made many helpful suggestions both during the work and in the preparation of the paper. This work was carried out during the tenure of the Armstrong College Fellowship.

---

* A. Schrammen, *Ann. d. Phys.* **83**, 1185 (1927).

THE SPECTRUM OF BARIUM FLUORIDE IN THE EXTREME RED AND NEAR INFRA-RED

BY THOMAS E. NEVIN, 1851 Overseas Student,
Imperial College of Science

Communicated by Prof. A. FOWLER, F.R.S., *May* 15, 1931.

ABSTRACT. A considerable number of new heads in the known system of bands in the extreme red, due to BaF, have been observed. A new system, also due to BaF, has been discovered in the near infra-red, and assigned to the transition $^2\Pi \rightarrow {}^2\Sigma$.

§ 1. INTRODUCTION

In Kayser's *Handbuch der Spectroscopie*, volume **7**, are given the wave-lengths of ten double-headed bands in the region λλ 6909–7431 observed by George* in a barium-fluoride arc and attributed by him to barium oxide. In the original paper are given, in addition, the wave-lengths of a number of bands of unknown origin between λ 7873 and λ 8224. The present paper gives an account of a further investigation of these bands. A photograph of the spectrum of the flame of a barium-hydroxide arc has failed to show any bands in the region λλ 6909–7431 but it exhibits some weak bands in the region λλ 7900–8500; these, however, do not agree in wave-length with the bands given by George. The spectrum of the barium-fluoride arc, on the other hand, has been found to exhibit a striking set of bands in the region λλ 6710–8750, of which the bands recorded by George undoubtedly form part. It therefore appears that these bands cannot have a barium-oxide origin but must be due to barium fluoride. This assignment is confirmed by an analysis of the bands. When this work was partly completed, it was found that the ten double-headed bands measured by George had already been ascribed to barium fluoride and that vibrational quantum numbers had been assigned to the heads by Johnson†. However, as many new bands in this system have been observed, the wave-lengths are recorded in the present paper.

§ 2. EXPERIMENTAL

The source for the production of the bands was an arc between carbon poles in air, fed with a current of 10 amp. from 220-volt mains. The lower and positive pole was hollow and packed with barium fluoride.

In the preliminary work a glass spectrograph having a dispersion of about 31 A.U./mm. at λ 6685 and 67 A.U./mm. near λ 8675 was used. In the region λλ 6600-

---

* W. George, *Zeit. für Wiss. Phot.* **12**, 237 (1913).

† R. C. Johnson, *Proc. R.S.* A, **122**, 161 (1929).

7700 panchromatic plates and plates stained with kryptocyanin were used. The former plates were not effective beyond λ 7200. In the infra-red from λλ 7600–8800, neocyanin plates, hypersensitized by bathing in dilute ammonia, were used. Plates for measurement were obtained in the first order of the 10-ft. grating which in this region has a dispersion of about 5·4 A.U./mm. An exposure of from half to one hour was sufficient with panchromatic and kryptocyanin plates. With a slit-width slightly greater than usual, a plate of the bands in the region λλ 7900–8750 was obtained on a neocyanin plate in about seven hours.

Table 1. Extreme red system of BaF, $^2\Sigma \rightarrow {}^2\Sigma$.

λ (in air)	i	ν (in vac.)	v', v''	λ (in air)	i	ν (in vac.)	v', v''
6715·81	2	14886·1	(2, 0)	7138·79	8	14004·0	(1, 1)
18·28	2	880·6		41·96	8	13997·8	
39·63	3	833·4	(3, 1)	61·63	5	959·4	(2, 2)
41·84	3	828·6		64·92	5	952·9	
54·58	3	800·6	(12, 9)	7359·21	3	13584·6	(0, 1)
56·90	3	794·9		63·28	3	577·1	
63·41	4	780·5	(4, 2)	81·66	4	543·3	(1, 2)
65·68	4	776·3		85·67	4	535·9	
87·16	4	729·6	(5, 3)	7404·18	5	502·1	(2, 3)
89·59	4	724·0		08·23	5	13494·8	
6810·62	3	14679·2	(6, 4)	26·92	6	460·6	(3, 4)
13·33	3	673·0		30·78	6	453·7	
35·36	2	625·7	(7, 5)	7449·73	5	419·5	(4, 5)
37·63	2	620·8		53·78	5	412·2	
59·98	2	14573·2	(8, 6)	72·54	4	13378·6	(5, 6)
62·95	2	566·9		76·08	4	372·2	
6909·33	4	14469·1	(1, 0)	95·80	3	337·0	(6, 7)
12·12	4	463·3		99·80	3	329·9	
32·49	5	420·8	(2, 1)	7519·01	2	13295·9	(7, 8)
35·15	5	415·3		23·40	2	288·1	
55·92	5	14372·5	(3, 2)	7661·22	2	13049·1	(2, 4)
58·70	5	366·5		—*	—	—	
79·40	4	323·9	(4, 3)	83·50	2	011·3	(3, 5)
82·07	4	318·4		88·34	2	003·1	
7002·29	3	14277·0	(5, 4)	—†	—	—	(4, 6)
05·75	3	271·0		7711·02	1	12964·8	
25·77	2	229·3	(6, 5)	28·56	1	935·5	(5, 7)
29·65	2	221·5		33·70	1	926·8	
7115·98	8	14049·0	(0, 0)	—	—	—	—
19·18	8	042·6		—	—	—	—

* Obscured by Ba line 7664·89.

† Obscured by Ba line 7706·58.

For convenience a spectrum of the iron arc in the second order was used for comparison. The error in this procedure was estimated by measuring the wave-length of first-order lines in terms of the second order, and it was found that it could be approximately corrected by subtracting 0·03 A.U. from the calculated wave-lengths. The wave-lengths of the ultra-violet and violet second-order lines were taken from Kayser's *Handbuch der Spectroscopie*, volume **7**, and the wave-lengths of the first-order infra-red lines from a paper by Meggers and Kiess‡.

---

‡ W. F. Meggers and C. C. Kiess, *Scientific Papers, Bureau of Stds*. No. 479 (1924).

§ 3. BANDS IN THE REGION λλ 6715–7734.

This system consists of five sequences of bands with double heads separated by about 6 cm.$^{-1}$. George has observed the (0, 0) and (1, 1) bands and four in each of the sequences $\Delta v = \pm 1$. The bands as already mentioned have been assigned to barium fluoride by Johnson. The wave-lengths, intensities, wave-numbers and vibrational quantum numbers are given in table 1. The intensities have been corrected, as far as possible, for the varying sensitivity of the photographic plates in this region by a comparison of spectra taken on panchromatic and kryptocyanin plates. The wave-numbers of the heads can be represented by the formulae:

$$\nu = 14064{\cdot}4 + 424{\cdot}46\,(v' + \tfrac{1}{2}) - 1{\cdot}805\,(v' + \tfrac{1}{2})^2 - 468{\cdot}75\,(v'' + \tfrac{1}{2}) + 1{\cdot}800\,(v'' + \tfrac{1}{2})^2 \quad \ldots\ldots(1),$$

$$\nu = 14070{\cdot}6 + 424{\cdot}33\,(v' + \tfrac{1}{2}) - 1{\cdot}945\,(v' + \tfrac{1}{2})^2 - 468{\cdot}16\,(v'' + \tfrac{1}{2}) + 1{\cdot}816\,(v'' + \tfrac{1}{2})^2 \quad \ldots\ldots(2).$$

Johnson considers that the less refrangible head of a pair is a Q head and that the bands arise from the transition $^2\Delta \rightarrow {}^2\Sigma$*. This suggestion seems scarcely feasible, as the transition violates the selection rule for the component of the electronic angular momentum in the direction of the internuclear axis, $\Delta\Lambda = 0$ or ± 1. It seems more probable that the bands are due to a $^2\Sigma \rightarrow {}^2\Sigma$ transition. Such a band would consist of two strong R and two strong P branches, the lines $R_1\,(K + \frac{1}{2})$ and $R_2\,(K - \frac{1}{2})$ forming a "natural" doublet and likewise the lines $P_1\,(K + \frac{1}{2})$ and $P_2\,(K - \frac{1}{2})$. On this assumption the two heads are the heads of the R branches.

§ 4. BANDS IN THE REGION λλ 7860–8750

A part of this system, up to λ 8224, has been measured by George. The bands are undoubtedly due to BaF. A number of the heads in George's list have not been recorded in the present work and they appear to be merely fortuitous condensations of fine-structure lines. The analysis leads to the conclusion that the bands are due to a $^2\Pi \rightarrow {}^2\Sigma$ transition. The data for the system are given in tables 2, 3 and 4. Assuming that the $^2\Pi$ doublet is normal, the component of shorter wave-length is $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$ and its companion $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$. The sequences $\Delta v = 0, \pm 1$ have been observed for the $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$ component. The distance between the R and Q heads in the $\Delta v = 0$ sequences is about 19·5 cm.$^{-1}$, and in the $\Delta v = -1$ sequence it is about 15 cm.$^{-1}$. The R heads in the $\Delta v = -1$ sequence have not been observed. The Q heads are exhibited in the form of v' and v'' progressions in table 3. The data for the $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$ component are not so complete. Seven Q heads in the $\Delta v = 0$ sequence have been measured, and three additional faint heads can be seen on the low dispersion plates. It is probable that the $\Delta v = +1$ sequence is present further in the infra-red but owing to the great drop in sensitivity of the plates beyond λ 8800 it cannot be measured, though on a very heavily exposed plate taken under low dispersion, bands can be very faintly observed in that region.

---

* The notation used in this paper is that recommended by Mulliken, *Phys. Rev.* **36**, 611 (1930).

Table 2. Wave-lengths and wave-numbers of heads $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$ component.

(v', v'')	Q head			R head			(v', v'')	Q head			R head			(v', v'')	Q head		
	λ (in air)	i	ν (in vac.)	λ (in air)	i	ν (in vac.)		λ (in air)	i	ν (in vac.)	λ (in air)	i	ν (in vac.)		λ (in air)	i	ν (in vac.)
(0, 0)	8151·03	8	12265·0	8136·99	7	12286·2	(1, 0)	7872·69	2	12698·6	7862·90	1	12714·4	(0, 1)	8472·10	2	11800·2
(1, 1)	8172·30	8	12233·1	8158·68	7	12253·5	(2, 1)	7895·04	1	12662·7	7885·02	1	12678·8	(1, 2)	8492·49	3	11771·9
(2, 2)	8193·64	8	12201·2	8186·44	6	12220·9	(3, 2)	7917·39	3	12626·9	7907·37	3	12642·9	(2, 3)	8513·02	4	11743·5
(3, 3)	8215·29	7	12169·1	8202·26	5	12188·4	(4, 3)	7939·14	3	12592·4	7929·77	3	12607·2	(3, 4)	8533·81	3	11714·9
(4, 4)	8237·12	6	12136·8	8224·55	3	12155·4	(5, 4)	7962·51	4	12555·4	7953·08	3	12570·2	(4, 5)	8554·60	3	11686·4
(5, 5)	8259·17	5	12104·5	8246·26	3	12123·4	(6, 5)	7985·66	4	12518·9	7975·98	3	12534·1	(5, 6)	8575·71	1	11657·7
(6, 6)	8281·15	4	12072·3	8268·62	2	12090·6	(7, 6)	8008·68	4	12483·0	7999·40	4	12497·5	(6, 7)	8597·4	1	11628·2
(7, 7)	8303·27	3	12040·1	8291·18	2	12057·7	(8, 7)	8031·28	4	12447·9	8022·56	3	12461·4	—	—	—	—
(8, 8)	8324·73	2	12009·0	8311·8	1	12027·8	(9, 8)	8054·96	3	12411·2	8045·88	3	12425·3	—	—	—	—
(9, 9)	8348·19	2	11975·3	—	—	—	(10, 9)	8080·09	4	12372·7	—	—	—	—	—	—	—
—	—	—	—	—	—	—	(11, 10)	8103·27	4	12337·3	—	—	—	—	—	—	—
—	—	—	—	—	—	—	(12, 11)	8125·51	2	12303·6	8116·82	2	12316·7	—	—	—	—

Table 3. v' and v'' progressions Q head $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$ component.

v'' v'	0		1		2		3		4		5		6		7		8		9
0	12265·0	464·8	11800·2		—		—		—		—		—		—		—		—
	433·6		432·9																
1	12698·6	465·5	12233·1	461·2	11771·9		—		—		—		—		—		—		—
			429·6		429·3														
2	—		12662·7	461·5	12201·2	457·7	11743·5		—		—		—		—		—		—
					425·7		425·6												
3	—		—		12626·9	457·8	12169·1	454·2	11714·9		—		—		—		—		—
							423·3		421·9										
4	—		—		—		12592·4	455·6	12136·8	450·4	11686·4		—		—		—		—
									418·6		418·1								
5	—		—		—		—		12555·4	450·9	12104·5	446·8	11657·7		—		—		—
											414·4		414·6						
6	—		—		—		—		—		12518·9	446·6	12072·3	444·1	11628·2		—		—
													410·7		411·9				
7	—		—		—		—		—		—		12483·0	442·9	12040·1		—		—
															407·8				
8	—		—		—		—		—		—		—		12447·9	438·9	12009·0		—
																	402·2		
9	—		—		—		—		—		—		—		—		12411·2	435·9	11975·3
																			397·4
10	—		—		—		—		—		—		—		—		—		12372·7

Some *Q* heads in the $\Delta v = -1$ sequence have been measured. The earlier heads in the sequence may be present in small intensity, but if so they are blended with the *R* heads of the $\Delta v = 0$ sequence of the $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$, the later members of which fall very near the positions in which the earlier *Q* heads may be expected. The measurement of the observed heads has been rendered somewhat difficult by the fact that they are obscured by fine-structure lines of the $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Sigma$ component. It is worthy of note that the *R* heads of this component have not been observed. The *Q* heads of the $\Delta v = 0$ sequence are strong and the *R* heads seem unlikely to be so faint as to escape observation. It seems more probable that the *R* branch turns back close to the origin, the resultant *R* head being blended with the *Q* head.

Table 4. *Q* heads of $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$ component.

λ (in air)	i	ν (in vac.)	(v', v'')	λ (in air)	i	ν (in vac.)	(v', v'')
8571·51	5	11663·4	(0, 0)	8337·21	4	11991·1	(4, 3)
8595·35	8	11631·0	(1, 1)	8359·12	3	11959·7	(5, 4)
8618·83	7	11599·3	(2, 2)	8383·80	3	11924·5	(6, 5)
8641·91	5	11568·3	(3, 3)	8408·51	3	11889·4	(7, 6)
8665·85	3	11536·4	(4, 4)	8433·83	2	11852·7	(8, 7)
8691·00	2	11503·0	(5, 5)	8459·27	2	11818·1	(9, 8)
8713·14	1	11473·8	(6, 6)	8484·53	2	11782·9	(10, 9)
8737·66	0	11441·5	(7, 7)	—	—	—	—

The wave-numbers of the *Q* heads of the two components can be represented by the following formulae:

$$\nu = 12281{\cdot}1 + 436{\cdot}70\,(v' + \tfrac{1}{2}) - 1{\cdot}818\,(v' + \tfrac{1}{2})^2 - 468{\cdot}71\,(v'' + \tfrac{1}{2}) + 1{\cdot}828\,(v'' + \tfrac{1}{2})^2 \quad \text{......(3)},$$

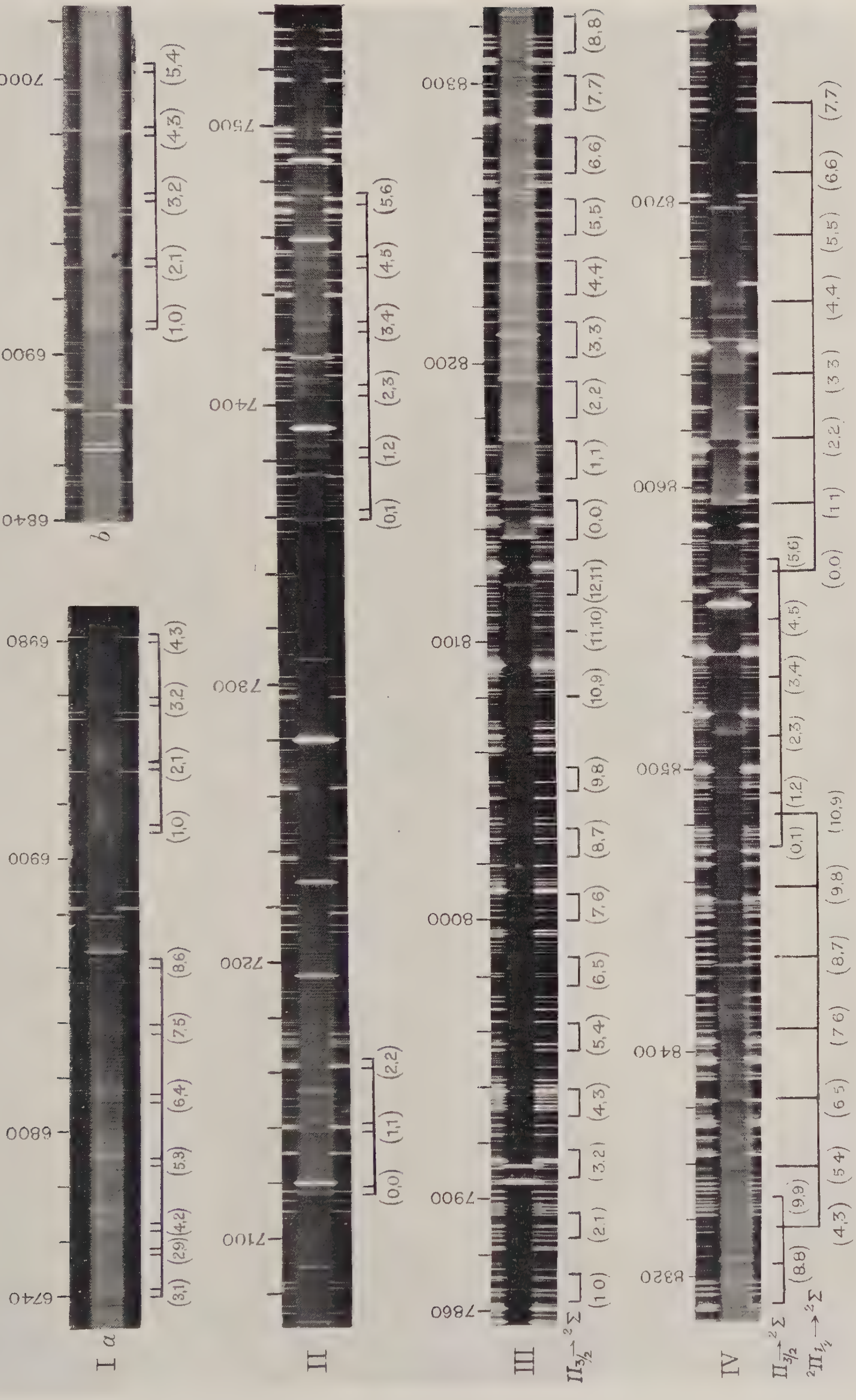
$$\nu = 11679{\cdot}0 + 438{\cdot}88\,(v' + \tfrac{1}{2}) - 1{\cdot}680\,(v' + \tfrac{1}{2})^2 - 470{\cdot}42\,(v'' + \tfrac{1}{2}) + 1{\cdot}450\,(v'' + \tfrac{1}{2})^2 \quad \text{......(4)}.$$

The accuracy of the latter formula is probably affected by the blending of the *R* and *Q* heads but the discrepancy seems outside the limit of error. Similar discrepancies are found in the analogous $^2\Pi \rightarrow {}^2\Sigma$ bands of CaF and SrF. The width of the $^2\Pi$ doublet is 602·1 cm.$^{-1}$ which is of the order of magnitude to be expected from an extrapolation from the known separation in the other alkaline-earth fluorides. Moreover, the formulae for the $\Delta v = 0$ sequences are almost exactly the same in the two components except for a constant term, and the assignment of the system to the transition $^2\Pi \rightarrow {}^2\Sigma$ seems reasonably certain.

It can be seen from a comparison of the formulae (1), (2), (3) and (4) that the two systems have the same final level. This level is also the final level of the well-known green bands of BaF.

§ 5. ACKNOWLEDGMENTS

My thanks are due to Prof. A. Fowler for his interest in this investigation, and to the Commissioners of the 1851 Exhibition for the award of a studentship which has made the work possible.



Spectrum of BaF λ6740–λ8750 photographed in first order 10 ft grating. I. $\Delta v = 0$ and -1 sequences of extreme red system: (*a*) panchromatic plate, exposure 2 hrs; (*b*) kryptocyanin plate, exposure 2 hrs. II. $\Delta v = 0$ and $+1$ sequences of extreme red system, exposure 45 min. III and IV. Infra-red bands, ${}^2\Pi \rightarrow {}^2\Sigma$ system, neocyanin plate, exposure 7 hrs.

THE REFRACTION AND DISPERSION OF GASEOUS PENTANE AND CHLOROFORM

By H. LOWERY, Ph.D., F.Inst.P., Head of the Department of Pure and Applied Physics, and T. S. HARTLEY, M.Sc.Tech.,
College of Technology, Manchester

Received May 9, 1931.

ABSTRACT. The refractive index of gaseous n-pentane is found to be 1·001683 for the green mercury line, λ 5461, the result being expressed in relation to the density of the gas. The dispersion over the range λ 4358–λ 6708 is represented by the Sellmeier equation: $(\mu - 1) = 14{\cdot}605 \times 10^{27}/(8978{\cdot}4 \times 10^{27} - \nu^2)$, where ν is the frequency of the incident light. Revised values for gaseous chloroform are:

$$\mu = 1{\cdot}001448 \text{ for } \lambda\ 5461 \quad \text{and} \quad (\mu - 1) = 15{\cdot}391 \times 10^{27}/(10933 \times 10^{27} - \nu^2).$$

§ 1. PENTANE

The only previous determination of the gaseous refractivity of pentane is that of Mascart*. He found that, for sodium light, the ratio of the refractivity of pentane to that of air is 5·82 at 12° C. Dufet† deduces from this that the refractive index under n.t.p. conditions is 1·001701, assuming the index for air to be 1·0002923. No previous determinations of the dispersion of pentane have been made.

The gaseous refractive index of normal pentane was determined in the present work for the green mercury line, λ 5461, by means of a Jamin interferometer and Hilger monochromatic illuminator, a mercury-vapour lamp being employed as source of light. The general arrangement of apparatus was similar to that already described in the case of carbon disulphide‡. The number of interference fringes displaced as the vapour gradually entered the refraction tube was observed, and the amount of vapour producing retardation of the light was estimated by means of the density bulb connected to the refraction tube.

Ten determinations of the refractivity of normal pentane for the green mercury line λ 5461 gave the values:

$(\mu - 1)_d \times 10^6$	1686, 1686, 1680, 1679, 1683, 1686, 1684, 1684, 1675, 1683;
Mean	1683.

---

* *Comptes Rendus*, **86**, 1182 (1878).
† *Recueil de Données Numériques* (1898).
‡ *Proc. Phys. Soc.* **38**, 470 (1926).

Here $(\mu - 1)_d$ denotes the refractivity in relation to the density, i.e. the values show the refractivity of gaseous pentane by the same number of molecules per unit volume as hydrogen contains at n.t.p.

The data employed in obtaining the reduced values were: C = 12·000, H = 1·008 and the density of hydrogen = 0·08985 gm./litre. These lead to the value 3·21 gm./litre for the theoretical density of pentane, the corresponding experimental value being 3·29 gm./litre.

The above value of the refractive index as determined for λ 5461 being assumed, the dispersion was measured over the range λ 4358–λ 6708 with the results shown in table 1. In these experiments the number of interference fringes counted was at least 600.

Table 1. Dispersion of gaseous n-pentane.

λ in Å.U.	$(\mu - 1)_d \times 10^6$ Observed	$(\mu - 1)_d \times 10^6$ Calculated	Difference
Li 6708	1663·7	1663·8	+ 0·1
Cd 6438	1666·8	1667·0	+ 0·2
Li 6104	1671·5	1671·7	+ 0·2
Hg 5770	1677·3	1677·2	− 0·1
Hg 5461	1683·0	1683·2	+ 0·2
Cd 5086	1691·8	1692·2	+ 0·4
Cd 4800	1699·9	1700·7	+ 0·8
Li 4602	1706·7	1707·5	+ 0·8
Hg 4358	1716·6	1717·3	+ 0·7

The values in the second column lead to the Sellmeier equation:

$$(\mu - 1)_d = 14{\cdot}605 \times 10^{27}/(8978{\cdot}4 \times 10^{27} - \nu^2),$$

where $(\mu - 1)_d$ represents the refractivity in relation to density and ν is the frequency of the incident light.

Comparison of the present measurements with the determination of Mascart may readily be made; thus the Sellmeier equation gives the value of $(\mu - 1)_d$ for sodium light (λ 5893) as 0·001675. On altering this in the ratio

$$\text{(experimental density at n.t.p.)/(standard density)} = 3{\cdot}29/3{\cdot}21,$$

the value of $(\mu - 1)$ under n.t.p. conditions is found to be 0·001717. This corresponds to Mascart's result as reduced by Dufet, 0·001701.

The refractivity of isopentane (boiling-point = 30° C.) also was obtained but while the value differs by 2½ per cent. from that obtained for normal pentane (boiling point = 37° C.) it was felt that a differential method of experiment would be more suitable in the study of the changes of refractivity among isomeric compounds, and the work is not, therefore, being followed up with the present apparatus.

§ 2. CHLOROFORM

Some results for the refraction and dispersion of gaseous chloroform have already been given*. Further experiments with various samples of chloroform give the most probable value of the gaseous refractive index of the substance in relation to the density as 1·001448 for λ 5461. With this revised value, the dispersion has been redetermined over the range λ 4358–λ 6708 as shown in table 2. The Sellmeier equation corresponding to the results in the second column is:

$$(\mu - 1)_d = 15{\cdot}391 \times 10^{27}/(10933 \times 10^{27} - \nu^2).$$

Table 2. Dispersion of gaseous chloroform.

λ in Å.U.	$(\mu - 1)_d \times 10^6$		Difference
	Observed	Calculated	
Li 6708	1433·9	1434·0	+ 0·1
Cd 6438	1436·2	1436·3	+ 0·1
Li 6104	1439·9	1439·6	− 0·3
Hg 5770	1443·5	1443·5	0·0
Hg 5461	1448·0	1447·7	− 0·3
Cd 5086	1454·7	1454·0	− 0·7
Cd 4800	1460·2	1459·9	− 0·3
Li 4602	1464·6	1464·7	+ 0·1
Hg 4358	1471·3	1471·5	+ 0·2

§ 3. ACKNOWLEDGMENT

Thanks are due to the Government Grant Committee of the Royal Society for a grant in support of the research.

---

* *Proc. Phys. Soc.* **40**, 26 (1927).

THE REFRACTION AND DISPERSION OF GASEOUS ETHYL BROMIDE

By H. LOWERY, Ph.D., F.Inst.P., Head of the Department
of Pure and Applied Physics, and J. K. ELLIOT, M.Sc.,
College of Technology, Manchester

Received May 9, 1931.

ABSTRACT. The refractive index of gaseous ethyl bromide in relation to density is found to be 1·001261 for the green mercury line, λ 5461. The Sellmeier formula representing the dispersion over the range λ 4358–λ 6708 is:

$$(\mu - 1) = 12{\cdot}407 \times 10^{27}/(10138 \times 10^{27} - \nu^2),$$

ν being the frequency of the incident light.

ONLY one determination of the refractivity of gaseous ethyl bromide is recorded, namely that of Mascart* who used a pressure method and found the refractivity relative to that of air at 12° C. for sodium light, λ 5893, to be 4·16. This result, when reduced to n.t.p. conditions, leads to the value of the refractive index as 1·001216, the assumed value for the refractive index of air being 1·0002924. The dispersion of gaseous ethyl bromide does not appear to have been studied previously.

The gaseous refractive index of ethyl bromide has been determined in the present work for the green mercury line, λ 5461, by means of a Jamin interferometer, Hilger monochromatic illuminator and mercury-vapour lamp as source of light. The number of interference fringes displaced was observed visually while the vapour was gradually allowed to enter one of the refraction tubes, the other tube being kept permanently evacuated. The amount of vapour producing retardation of the light was estimated by means of a density bulb connected to the refraction tube.

The results of ten determinations of the refractivity for λ 5461 are as follow:

$(\mu - 1)_d \times 10^6$	1258, 1257, 1262, 1261, 1261, 1257, 1262, 1263, 1265, 1268;
Mean	1261,

where $(\mu - 1)_d$ represents the refractivity in relation to the density, i.e. the results show the refractivity of gaseous ethyl bromide by the same number of molecules as 1 cm.^{3} of hydrogen contains at n.t.p.

---

* *Comptes rendus*, **86**, 1182 (1878).

Dispersion measurements over the range λ 4358–λ 6708 gave the results shown in the table; these were made relative to the refractivity determination for λ 5461 given above. The observed values of the second column, treated by the method of least squares, give the Sellmeier equation:

Dispersion of gaseous ethyl bromide.

λ in Å.U.	$(\mu - 1)_d \times 10^6$		Difference
	Observed	Calculated	
Li 6708	1249·1	1248·4	− 0·7
Cd 6438	1250·1	1250·6	+ 0·5
Li 6104	1253·7	1253·7	0·0
Hg 5770	1257·0	1257·3	+ 0·3
Hg 5461	1261·3	1261·4	+ 0·1
Cd 5086	1267·2	1267·3	+ 0·1
Cd 4800	1273·0	1272·8	− 0·2
Hg 4358	1283·4	1283·8	+ 0·4

$$(\mu - 1)_d = 12{\cdot}407 \times 10^{27}/(10138 \times 10^{27} - \nu^2),$$

ν being the frequency of the light.

Thanks are due to the Government Grant Committee of the Royal Society for a grant in support of the research.

TWO PRECISION CONDENSER BRIDGES

By ALBERT CAMPBELL, M.A.

Received June 17, 1931.

ABSTRACT. In Heydweiller's modification of the Carey Foster bridge as ordinarily used (with variable mutual inductance) the capacitance of the condenser can be read directly, but the power-factor has to be deduced by calculation. To facilitate direct reading of both capacitance and power-factor the author has developed two bridge systems, *A* and *B*, based on that of Carey Foster. In both of these a fixed mutual inductance *M* is used and there is no added resistance in the condenser arm.

The capacitance $C \doteqdot M/PR$, where *P* and *R* are the resistances of the other two arms. To give direct reading for *C*, *P* can be varied in simple steps (e.g. 10, 100, 1000, 10,000), giving range multipliers, while *R* consists of a conductance box reading in millimhos. In system *A* a fourth arm *Q* of variable low resistance is added to the bridge. The power-factor is given by $Q/M\omega$ and can be read directly (at given pulsatance ω) if a slide wire is used for *Q*. In system *B* the power loss in *C* is balanced by the addition of impurity to the mutual inductance *M* by means of a closed-loop circuit variably coupled to both the primary and secondary coils of *M*. When the resistance of this loop circuit is set proportional to the frequency, the scale of the double inductor which varies the couplings can be graduated to read the power-factor directly. When a simple amplifier is used in the detector circuit, a capacitance range of 100 $\mu\mu$F up to 10 μF can be obtained and a power-factor range from 0·0001 to 0·01 with high accuracy of reading.

§ 1. INTRODUCTORY

For the measurement of the capacitance and power-factor of condensers over a wide range of values the Carey Foster method with Heydweiller's modification is, without doubt, one of the simplest and most accurate. The standards of reference, being resistance and mutual inductance, can be constructed to have high accuracy and good permanence. By using a variable mutual inductance the capacitance can be read directly, but unfortunately the power-factor requires to be calculated from observed numbers. To avoid this difficulty the author has developed from the Carey Foster bridge two new bridge systems* which are direct reading for both capacitance and power-factor. They may be designated (*A*) Slide-wire system and (*B*) Closed-loop compensator system.

§ 2. SLIDE-WIRE SYSTEM (*A*)

C
s
P, *Q*, *R*

The *A*-system is a four-arm bridge, as shown in figure 1, in which *C* is the capacitance to be measured and *s* the internal resistance representing its power loss. It is a simple Carey Foster system with the addition of a fourth arm *Q*, and without added resistance in the *C* arm. The resistances *P*, *Q* and *R* are variable and the

---

* British Patent Specifications, No. 317,642 and No. 350,789.

M, L, q
ω

mutual inductance M is fixed. Let the P arm have self-inductance L, and let q be the power-factor of C at pulsatance ω;

then $$q = C\omega s.$$

It can then be shown that, for balance,

$$C = M/(PR - Qs) \qquad \text{......(1)},$$

and $$\text{power-factor } q = \frac{Q}{M\omega} + \frac{(L-M)\,\omega}{P - Qs/R} \qquad \text{......(2)}.$$

Let Q be so small compared with R that Qs can be neglected. The equations then become

$$C \doteqdot M/PR \qquad \text{......(3)},$$

and $$q \doteqdot Q/M\omega + (L-M)\,\omega/P \qquad \text{......(4)}.$$

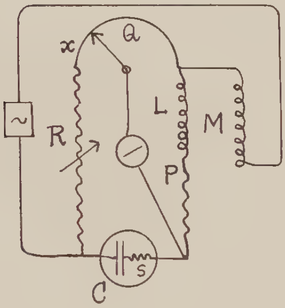


Fig. 1. System *A*.

Usually L is made equal to M, in which case

$$q \doteqdot Q/M\omega \qquad \text{......(5)}.$$

In practice the approximations in equations (3) and (5) can be made very close to exactness.

In order that C may be read without calculation, the value of M is made an integral power of 10 (e.g. 1 mH) and the arm R consists of a conductance box reading in millimhos, while P can be arranged to go in steps such as 10, 100, 1000, 10,000 Ω, giving a series of ranges for C.

For a given value of ω, q is directly proportional to Q. This latter is conveniently made a slide-wire, which can be graduated to read q directly for a standard value of ω.

For other frequencies a multiplying factor is required. The total resistance of the slide-wire is made so small, relatively to R, that the part x in the R arm is negligible except in extreme cases. Power-factors outside the normal range can be determined by altering L by known amounts, so that $L - M$ is no longer zero, and calculating by equation (4).

Complete instruments have been built on this system giving, with two values of M, a range of capacitance-measurement from 1 $\mu\mu$F up to 10 μF, and reading power-factor directly at frequencies of 50 and 800 cycles per sec. from 0·0001 up to 0·01. But system B is more convenient, as it is quite direct reading over a long range of frequencies.

§ 3. CLOSED-LOOP COMPENSATOR SYSTEM (B)

μ, m
ρ, λ

The B-system is shown in figure 2. It consists of an ordinary Carey Foster bridge without external resistance in the C arm, but with a closed loop H coupled to the primary and secondary coils of the fixed mutual inductance M by means of mutual inductances μ and m which are both variable. The total resistance and self-inductance of the loop are ρ and λ respectively, λ being constant and ρ variable.

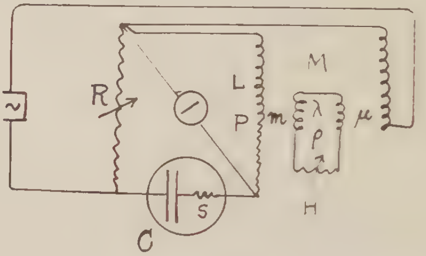


Fig. 2. System B.

A closed circuit of this kind may be called an "M-compensator," for it can be used to adjust the impurity of a mutual inductance, reducing it to zero if desired*, as m and μ can have the same or opposite signs. When the bridge is balanced we have

$$M\lambda - m\mu/CR = P\lambda + (L - M)\,\rho - M\rho s/R \qquad \text{......(6),}$$

and

$$M/CPR = 1 - (\omega^2/P\rho)\,[(L - M - Ms/R)\,\lambda + m\,(m - \mu) + m\mu s/R] \qquad \text{......(7).}$$

In this particular application M is usually made equal to L, and ρ is always much greater than $\lambda\omega$. With these conditions, when the bridge is balanced, we have

$$\text{power-factor } q = Cs\omega \risingdotseq m\mu\omega/M\rho \qquad \text{......(8),}$$

and

$$M/C \risingdotseq [P + m\,(m - \mu)/\rho]\,R - m\mu\omega^2 s/\rho \qquad \text{......(9).}$$

By suitable choice of m, μ and ρ the last term in equation (9) can be made negligible compared with PR, and thus

$$M/C \risingdotseq [P + m\,(m - \mu)/\rho]\,R \qquad \text{......(10).}$$

In the practical instrument m and μ are varied together so as to be always nearly equal except when both are small. In this way we can ensure that the $m(m - \mu)$ term shall be negligible and then

---

* For other applications, see A. Campbell, *Proc. Phys. Soc.* **29**, 347 (1917) and British Patent Specification No. 294,053.

$$C \doteqdot M/PR \qquad \text{......(11).}$$

As in system A, the capacitance is read directly, a conductance box being used for the arm R. To make the power-factor readings direct, the frequency is observed and ρ is set proportional to it, say

$$k\rho = \omega.$$

Then $$q = km\mu/M = m\mu \times \text{const.} \qquad \text{......(12).}$$

The variation of μ and m is carried out by means of a little inductometer whose fixed coils are in the primary and secondary M-circuits, while the rotatable coil is in the loop circuit. The scale is marked proportionally to $m\mu$ and reads q directly.

The actual instrument, which is made by the Cambridge Instrument Company, has a capacitance range from 10 μF down to 100 $\mu\mu$F, with $M = 1$ mH, but much smaller values can be measured by taking differences. Within the frequency range of 50 to 2000 ∼ it reads power-factors directly from 0·01 down to 0·0001. The detecting instrument can be either a vibration galvanometer or a telephone, according to the frequency used. For the smaller capacitances, below 0·1 μF, it is desirable to use an amplifier in the detecting circuit. With a simple amplifier and moderate power from the source it is possible to read the capacitance over the whole range to about 1 part in 10,000, and the power-factor to about 0·0001.

§ 4. CONDUCTANCE BOX

The high accuracy of reading is attained by the use of the specially designed conductance box which forms the R arm. This consists of a number of variable resistances in parallel, beginning with three step-switch dials which give consecutive resistances of

(1) ∞, 100, 50, 33·33, 25 ... ... 11·111, 10 Ω,
(2) ∞, 1000, 500, 333·3, 250 ... ... 111·11,
(3) ∞, 10000, 5000, 3333, 2500 ... ... 1111·1, 11000 Ω,

thus affording a range of 0 to 100 millimhos in steps of 0·1 millimho. It should be noticed that it is practically impossible to provide continuous adjustment down to zero, but a 1 : 100 range is here convenient. To continue this parallel-step system for finer adjustment would involve sets of resistance coils mounting up to megohms, which would be costly and troublesome. To avoid this difficulty, two more circuits D and E are added in shunt, each of the order of 500 Ω. D is a single step-switch giving

0·50, 0·51, 0·52 ... ... 0·60 mmho (2000 Ω down to 1666·7 Ω), and *E* consists of two step-switches and a slide-wire, all in series, giving

0·50000, 0·50001 ... ... 0·51000 mmho (2000 Ω down to 1960·8).

D and *E* thus keep a minimum value (0·1 mmho) always in circuit, and this is taken account of by marking dial (2) with 1, 2, 3 ... 10 mmhos instead of 0, 1, 2, 3 ... 10 mmhos. Then dials (4), (5), (6) and (7) are marked 0·01, 0·02, 0·03 ...; 0.001, 0·002, 0·003 ... and so on.

In the *E* circuit the small conductance-variations made by the series switches do not add quite accurately, but the error is negligible. Even the minimum value (1 mmho) can be read with high accuracy.

MAGNETOSTRICTION AND HYSTERESIS

By W. N. BOND, M.A., D.Sc., F.Inst.P.,
Lecturer in Physics in the University of Reading

Received June 17, 1931. *Read at the meeting held at Reading, June* 20, 1931.

ABSTRACT. The magnetostriction of unannealed wrought iron is measured, by means of an optical lever of length 0·12 mm., up to an intensity of magnetization of 985 e.m.u. The longitudinal extension and the intensity of magnetization are measured for a cycle of magnetization, both being found to show hysteresis. The extension is approximately proportional to the square of the intensity but seems to depend slightly on the previous magnetic history as well as on the intensity of magnetization. This hysteresis indicates that the extension is a consequence of the magnetization, in the same sense that the magnetization is a consequence of the applied field.

For a bibliography of papers on magnetostriction since its discovery by Joule and investigation by Shelford Bidwell reference may be made to *The International Critical Tables*.*

In the present experiments the longitudinal extension of a wrought-iron bar when magnetized was measured by means of an optical lever such as I have described previously†. The iron bar was 82·7 cm. long and 0·78 cm. in diameter. To its ends brass extension-pieces were soldered, and the bar was placed in a long vertical solenoid, having 19·3 turns per cm. The lower brass piece rested in a "geometrical constraint" in a brass disc cemented to the floor. The lever had its outer legs resting on the pole-pieces of a small strong horse-shoe magnet which was supported on a slate bracket let into the wall. The third leg of the lever rested on the upper brass extension-piece. The length of the lever, $0{\cdot}12_1$ mm., was only estimated approximately by direct measurement, but was found accurately by comparison with a less sensitive lever of length 1·41 mm. Deflections of the lever were measured by a simple lamp-and-scale method, the scale distance being 99·4 cm. The magnification of the lever was thus 16,400-fold. An extension of the specimen by one millionth of its length, i.e. $8{\cdot}27 \times 10^{-5}$ cm., gave a scale reading of 1·36 cm. A change in length by 1 in 136,000,000 would be just detectable on the scale.

To make full use of the large magnification, it would be necessary to keep the temperature of the bar of iron constant to within about 1/1000° C. In the present experiments no thermostat was used, but the readings were taken in rapid succession and a correction was applied for the gradual change of zero. The accuracy thus attained is of the order 1/20,000,000 of the length of the specimen. Since a maximum scale-reading of 5·85 cm. was obtained, the percentage error in the reading of this scale was little, if any, greater than the percentage error in the reading of the scale of the ammeter in series with the solenoid.

---

* *Int. Crit. Tables*, **6**, 441. See also W. L. Webster, *Proc. Phys. Soc.* **42**, 435 (1930).

† *Phil. Mag.* **7**, 1166 (1929).

With the specimen supported by the floor, and the measuring apparatus supported from the wall, it was found necessary to carry out the experiments without anyone walking within about two metres of the apparatus.

$\delta l/l$, I The longitudinal extension $\delta l/l$ and the intensity of magnetization I were measured for applied fields of from 0 to 31·7 gauss, and also for cycles of magnetization with a maximum applied field of 31·7 gauss. The intensity of magnetization I was measured by a magnetometer method, a simple declination magnetometer being used with a lamp and scale, and a coil to compensate for the effect of the field of the solenoid on the magnetometer. The results of these experiments are given in figures 1 and 2. In both of these diagrams the results are plotted against

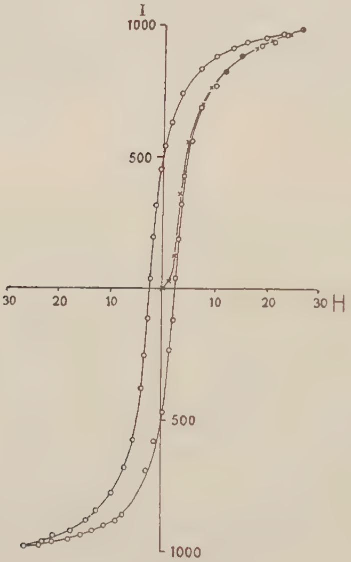


Fig. 1.

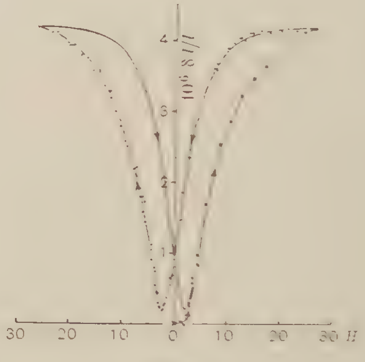


Fig. 2.

H the magnetizing field H, which has been deduced by deducting the demagnetizing field from the applied field. A demagnetizing coefficient of $0{\cdot}005_4$ was assumed.

In figure 3 the fractional extension $\delta l/l$ is plotted against the intensity of magnetization I. In figures 2 and 3, the measurements have for clearness all been inserted on one half of the hysteresis curve. The experiments were not accurate enough to detect any difference between the shapes of successive cyclic curves.

It was found, figure 2, that when the coercive-force field was applied the iron bar did not become quite as short as when the specimen was properly demagnetized. Figure 3 shows that for small intensities of magnetization the extension is approximately proportional to the square of the intensity. This diagram also shows that the specimen returns to its original length only when properly demagnetized. The diagram shows other hysteresis effects, the magnetostriction depending not only on the intensity of magnetization but also on the previous magnetic history of the specimen. The vertical arrow in figure 3 indicates the remanent magnetization and magnetostriction.

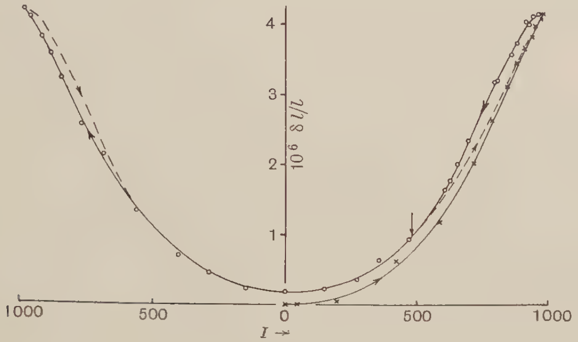


Fig. 3.

The direction in which the hysteresis loops in figure 3 are traversed indicates that the longitudinal extension, or magnetostriction, is a consequence of the intensity of magnetization, in the same sense that the intensity is a consequence of the applied magnetic field.

In conclusion I should like to thank Prof. J. A. Crowther for the interest he has taken in these experiments.

ON THE MEASUREMENT OF THE TOTAL HEAT OF A LIQUID BY THE CONTINUOUS MIXTURE METHOD

By H. R. LANG, Ph.D., F.Inst.P.,

Imperial College of Science and Technology

Received May 12, 1931.

ABSTRACT. A development of Callendar's continuous-mixture method for the measurement of the total heat or specific heat of a liquid is given. It consists of the determination of the amount of heat extracted by a stream of water from a hot stream of the liquid. A discussion of the heat losses and the method of reducing and allowing for these is included, as well as experimental tests of the theory of the method.

§ 1. INTRODUCTION

In recent years attention has repeatedly been directed to the demand for experimental data that will help in the attempt to produce a rational system of equations representing the thermodynamic properties of substances in liquid and vapour states. This is important not only for testing various theories, but also in many industrial problems. Such a system has been devised for the properties of water and steam by Callendar and others, and the use of steam tables is familiar to engineers.

With the assistance of the Institution of Petroleum Technologists an attempt is now being made to obtain such measurements for petroleum oils. Following the methods used by Callendar, the continuous electric method* was first used, and recently the continuous mixture method† has been suitably modified for use at temperatures at which the electric method is more troublesome. The object of the present paper is to describe this modified method, with particular reference to its use for oils, and the method of eliminating the heat loss.

§ 2. THE TOTAL HEAT

In practical calculations the quantity usually required is the change of total heat, and it is this that has to be calculated from the specific heat data. The advantage of the present method is that it directly measures this change over any range of temperature desired, and by the introduction of suitable throttles can be used over any range of pressure‡. Thus the energy-change per unit mass of the substance in passing from one set of conditions to another is directly measured and tabulated. Usually, to obtain this information an uncertain calculation has to be made, in which a knowledge of the specific heat and its change with temperature is required, as well as certain other thermal properties of the substance. An example will make this clear. A quantity frequently required is the amount of heat necessary to change a liquid at one temperature and pressure to a vapour at another temperature and pressure. This is the difference of total heat between the two cases, and is obtained by simple subtraction, in place of the more usual intermediate steps which involve uncertainty.

---

* H. L. Callendar and H. T. Barnes, *Phil. Trans.* A, **199**, 55 (1902); H. R. Lang, *Proc. R.S.* A, **118**, 138 (1928).

† H. L. Callendar, *Phil. Trans.* A, **212**, 1 (1912).

‡ H. L. Callendar, *Howard Lectures*, R.S.A. (1926).

The variation of the specific heat of many liquids with temperature is quite complex, and unless some form of integrable equation can be fitted to the curve it is only possible to obtain the mean specific heat over a range by a graphical method, or by making an approximate equation to the curve. By the use of the total heat tables such a mean specific heat, if it is required, can be found by dividing the change of total heat between the two temperatures by the corresponding temperature difference.

§ 3. ELEMENTARY THEORY

The principle of the method is to measure the amount of heat extracted from a hot stream of the liquid by a cold stream of water. The necessary measurements are the rise in temperature of the water and the fall in temperature of the liquid, as well as the rate of flow of each stream. As in all other calorimetric experiments it is only possible to measure changes of total heat, so that, in order to find the value at the higher temperature (inflow), it is necessary to know that at the lower temperature (outflow). Let H_1 and H_2 be the total heat of the liquid in cal./gm. at the temperatures t_1 and t_2 respectively; H_1, H_2 t_1, t_2

s the mean specific heat of water in cal./gm.-deg. between the temperatures t_3 and t_4; s

t_3 the inflow temperature of the water; t_3

t_4 the outflow temperature of the water; t_4

m the rate of flow of the liquid (oil) in gm./sec.; m

M the rate of flow of the water in gm./sec.; and let $d\theta = (t_4 - t_3)$. M, $d\theta$

Then the energy equation per second is:

$$(H_1 - H_2)\, m = sMd\theta + \text{heat losses} \qquad \ldots\ldots(1).$$

§ 4. THE APPARATUS

The main features of the apparatus have been described in an earlier paper*, and only a brief outline will be needed here. The heat-exchanger, which is shown in figure 1 without the external jacket, consists of a central tube along which is passed a central rod carrying a spiral to cause good circulation of the oil. The annular space between the rod and the tube is about $\frac{1}{8}$ in. The water enters at the bottom, passes up the outside of the internal lagging, and then washes the outside of the central oil tube, and leaves again at the bottom. The internal lagging is of asbestos placed between two brass tubes. Special provision is made for the relative expansion of the various parts of the exchanger, and also for the escape of any air that may find its way into the apparatus. The exchanger is mounted vertically and is about three feet in length. The temperature rise of the water is measured with a differential pair of platinum resistance thermometers, reading to thousandths of a degree centigrade. The temperature of the oil is also measured with platinum resistance thermometers. Jacketed thermometer pockets of the type used by Callendar* are utilized to make the heat losses from them independent of the flow-rate.

---

* H. R. Lang, *J. Inst. Petr. Techn.* **16**, 792 (1930).

Both flow circuits are fed from overflow devices; the rate can be varied for the oil by means of glass capillary-tube throttles, and for the water by raising or lowering the height of the overflow chamber. Experiment showed that the inflow temperature of the oil could safely be taken as that of the thermostat bath from which it passes into the exchanger. This bath is controlled by a modified form of recorder in conjunction with a resistance thermometer†, and its temperature varied by less than 0·03° C. even at the highest temperatures used (250° C.). The connecting tube between the spiral of pipe immersed in this bath and the heat-exchanger was made as short as possible in order to minimize the heat-loss from this region.

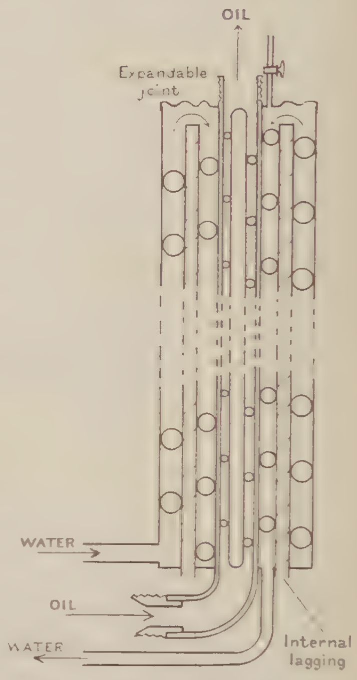


Fig. 1. The heat-exchanger.

§ 5. METHOD OF ELIMINATING THE HEAT-LOSS

In considering the heat-losses from the apparatus it has to be remembered that the temperatures of the water stream and the outflow temperature of the oil stream are never very different from the surrounding temperature. In its present form it has been possible to reduce the heat-loss from the apparatus to about 2 per cent. on the fast flows, and a correspondingly larger percentage on the slower ones, since the heat-loss itself is independent of the flow. The greater part of the loss is from the water stream and is dependent only upon its rise in temperature $d\theta$, provided the temperature-distribution over the apparatus is independent of the rate of flow. By surrounding the heat-exchanger with a jacket fed from the same tank of water, the external temperature is always maintained the same as the inflow temperature. The loss from the water may be written,

---

* H. L. Callendar, *Phil. Trans.* A, **212**, 16 (1912).

† H. R. Lang, *Proc. Phys. Soc.* **42**, 589 (1930).

$$\text{heat-loss} = f(d\theta, M).$$

The terms in M have been included to allow for the possibility of a change in temperature-distribution due to conduction with change in flow, and are known to be very small. As a first approximation we may therefore write,

$$\text{heat-loss} = k_1 \, d\theta,$$ k_1

as far as the part lost from the water stream is concerned. In the earlier experiments there was a comparatively large and uncertain heat leak from the connecting pipe between the thermostat bath and the exchanger. This loss has been reduced and made quite definite and measurable in the following way. The pipe is lagged with asbestos, over the outside of which is fixed a heavy copper cylinder B, figure 2. This serves to distribute the heat generated by the passage of an electric current through a coil wound on the cylinder and suitably insulated from it. The power supplied to the coil is varied so as to maintain a zero reading of a thermocouple, one junction of which is fixed to the copper cylinder while the other junction is in the thermostat bath. The outside of the lagging is therefore always at the same temperature as the inside, but a new difficulty is thereby introduced, namely that heat is able to creep along the pipe itself and so into the water, thus causing the temperature-rise of the water to be a little too large. Thus, in order to reduce the heat-loss from the oil, the radial temperature-gradient A–B, figure 2, from the centre of the pipe to the outside of the surrounding lagging must be reduced. This, however, changes the axial gradient C–D and thereby increases the conduction into the water stream. These two effects are antagonistic. It was found best to reduce to zero the loss from the oil by maintaining the radial gradient at zero, and to measure and allow for the conduction into the water stream. By making this connecting pipe as thin as possible and of a bad conductor (German silver) this negative heat-loss was reduced to the order of 2 per cent. of the total heat exchanged

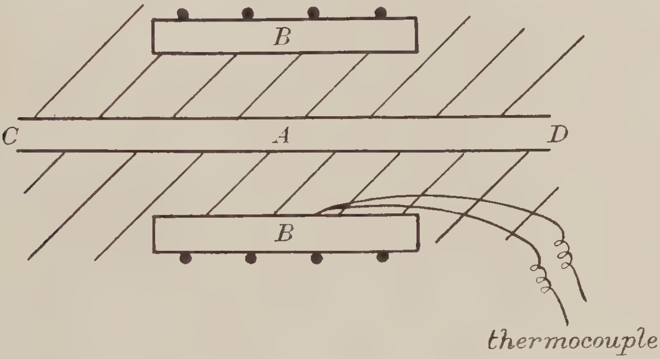


Fig. 2. Lagging of the connecting pipe.

in the experiments. By taking "a cold reading*" (i.e. the rise in temperature of the water stream when no oil is flowing, all other conditions being the same) and subtracting this from that found when the oil is flowing, this loss, together with other small conduction losses, is eliminated. This involves the assumption that the temperature gradients remain the same. Such an assumption was made in a similar case by Regnault†, in his classical experiments on the specific heat of gases at constant pressure. This has been criticized by Swann‡, who considers that this would give too low a value. The special feature of the present method, devised to overcome the difficulty, is that the gradients are maintained the same, in the manner described above. The radial gradient is always zero, and the axial gradient is sufficiently nearly the same when the oil is flowing as when it is not. For one end C of the pipe, figure 2, is in the thermostat bath, and the other D is washed by the cold stream of water immediately on entering the exchanger. It is this end of the pipe that may possibly change in temperature when the oil flow is turned on, but the experimental tests of the method given below show that the change may safely be neglected. It was found that the cold readings varied inversely as the rate of flow M, and the explanation is simple. If the temperature-distribution is independent of the rate of flow then we have

$$\text{heat absorbed by water} = Msd\phi = \text{constant},$$

$d\phi$, s where $d\phi$ is the "cold reading" and s the specific heat of water; and as the specific heat of water over this short range may be considered constant it follows that

c

$$d\phi = c/M, \text{ where } c \text{ is a constant.}$$

A typical set of "cold reading" lines is exhibited in figure 3, and the temperature of the thermostat bath is written along each of the lines. Except for work of the highest precision, it suffices then to observe "a cold reading" for one rate of flow, and from the line drawn through this point and the origin to read off the appropriate value for other rates of flow.

In any experiment (set of flows) since the inflow temperature is constant and quite independent of the flow, and since the rise in temperature of the water is arranged to be the same for different flow-rates, the temperature-distribution over the apparatus will be almost the same in each case, and thus the heat-loss from the oil stream will be constant and independent of the rate of flow, and small compared to that from the water stream. Moreover, as the temperature-rise of the water ($d\theta$) is nearly enough constant throughout the experiment, this loss may conveniently be expressed in the form,

k_2

$$\text{loss from oil stream} = k_2 d\theta + f(m, d\theta).$$

The additional terms have again been included as a reminder of the possibility of small changes of temperature-distribution with flow. The full equation for the heat-exchange per second may now be written:

---

* H. T. Barnes, *loc. cit.* p. 195.

† *Mémoires de l'Académie des Sciences de l'Institut Impérial de France* (1862).

‡ W. F. G. Swann, *Phil. Trans.* A, **210**, 231 (1910).

$$(H_1 - H_2)\, m = sMd\theta + k_1\, d\theta + k_2\, d\theta + f(m, M, d\theta) \qquad \ldots\ldots(2),$$

neglecting for the present the end terms, and writing

$$z = k_1 + k_2,$$ z

we have

$$H_1 = H_2 + sd\theta M/m + zd\theta/m \qquad \ldots\ldots(3),$$

or

$$Y = (H_1 - H_2)\, m/d\theta M = s + z/M \qquad \ldots\ldots(4).$$ Y

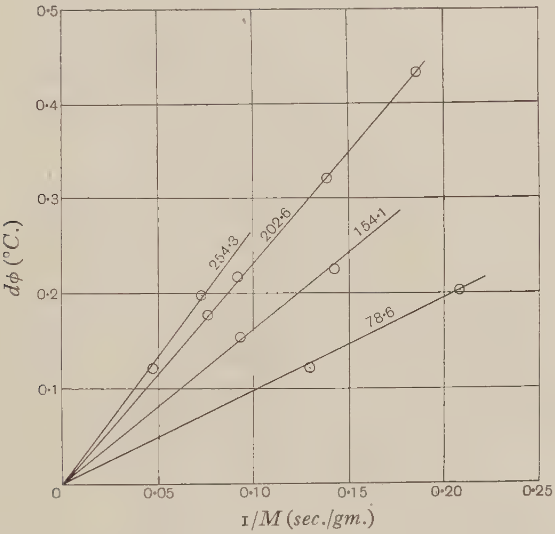


Fig. 3. Typical cold-reading lines.

If then the small terms dependent upon the flow-rates are negligibly small, and if the other assumptions made are to be experimentally justified, a plot of Y against $1/M$ should be linear. Before the present form of the apparatus was proceeded with some preliminary experiments were made with water in both flow circuits and with a fourfold change of flow-rate. The experimental points were colinear to rather better than 1 part in 1000. In this case the values of H_1 and H_2 were taken from the standard tables for water. The apparatus was therefore developed along these lines, and the following additional test was devised. Equation (3) may be written

$$H_1 = A + zd\theta/m \qquad \ldots\ldots(5),$$

where

$$A = H_2 + sd\theta M/m \qquad \ldots\ldots(6).$$ A

The quantity A represents the total heat uncorrected for heat-loss, and will therefore depend to some extent on the rate of flow. It should be noted that only the ratio M/m of the two flows is required accurately, and the actual value of m is needed only approximately for the calculation of the small heat-loss term. The advantage of this is that the exact time of switching over the flows into the collecting flasks need not be known, as being mechanically coupled they are switched simultaneously. Further, as the densities of the oil and water are of the same order, the correction to the ratio of the weights on account of buoyancy becomes vanishingly small. Since H_1, the total heat at the inflow temperature of the oil, is constant in any one experiment, a test of the above equation is provided by plotting the quantity A against $d\theta/m$. As z is small the value of A does not change very much from flow to flow, so that it is possible to use a very open scale. It has been found that for all the experiments so far tried this equation holds to an order of accuracy even better than the estimated observational accuracy, provided the flows are turbulent. Some typical "A curves" are shown in figure 4, and in order to save space a constant has been subtracted from the values of A. This and the temperature t_1 are given on the figure. The intercept on the ordinate axis gives the value of the total heat H_1 less the appropriate constant, and the slope gives that of z. The value of H_2 has been obtained in each case from the integration of the specific heat/temperature curve found by the continuous electric-flow method*. It is usual to take the total heat as zero at 0° C., and this forms the convenient arbitrary zero. When reckoned from this point H_2 is small compared to the second term in equation (3), and it is not therefore required to any great accuracy. Further, as the temperature t_2 does not vary by more than about 15° C. from laboratory temperature, it is only necessary to know the variation of the total heat of the substance over a short range of temperature, in order to be able to calculate the value of H_1.

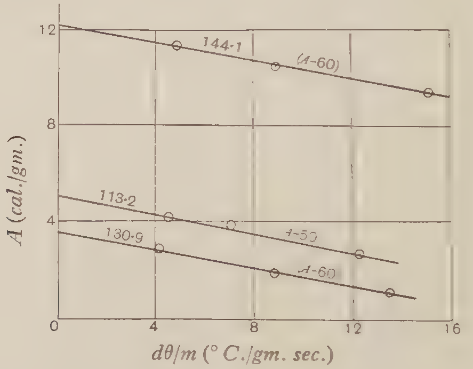


Fig. 4. Typical curves for A

§ 6. METHOD OF REDUCTION OF RESULTS

The rise $d\theta$ in temperature of the water is calculated from the mean of a series of "cold" and "hot" readings, and is reduced to the gas scale in precisely the same way as for the experiments by the electric-flow method*. The value of A, equation (6), is next calculated, and when a "run" has been repeated the average is taken at this stage. In the earlier experiments the heat-loss term z was eliminated between two equations of the form (6) for a fast and a slow flow. When an intermediate one had been used this value of z was substituted in the third equation. The two values of H_1 found in this way agreed in general to 1 part in 600. An abridged set of observations is given in table 1, which shows the magnitude of the various quantities to be measured and the agreement between "runs."

---

* H. R. Lang, *Proc. R.S.* A, **118**, 141 (1928).

Table 1. Abridged set of observations.

"Miri" fraction No. 4. Total heat at t_1 = 131·55° C.							
t_2	t_3	$d\theta$	m	M	H_2	A	H_1
° C.			gm./sec.		cal./gm.		
18·50	17·98	7·703	0·7064	4·858	8·092	61·067	—
18·50	17·98	7·691	0·7031	4·852	8·092	61·166	—
22·12	17·84	7·904	2·0432	13·921	9·715	63·568	64·94
22·10	17·84	7·886	2·0317	13·885	9·706	63·601	—
19·52	17·82	7·789	1·2993	9·077	8·547	62·962	—
19·54	17·82	7·747	1·2987	9·132	8·557	63·031	65·09

Mean value: H_1 = 65·01 cal./gm.; z = 0·351 cal./° C.

A series of determinations of the specific heat of this oil had previously been made by the electric-flow method up to 100° C. and, by integration and extrapolation in the equation that had been fitted to these results, a value of 64·97 cal./gm. was obtained for the total heat at this temperature. This close agreement of values obtained by two entirely different methods, which is typical of many cases, shows that any constant errors that may exist can safely be neglected.

From a large number of experiments that have now been performed with this apparatus, it has been found that the small variation in the value of the heat-loss per degree (z), is independent not only of the rate of flow but also of the rise in temperature of the water. A fourfold range of flows and a twofold range of temperature-rise have been tried. The value of z is calculated from the difference between two large and nearly equal quantities, and consequently an error of 1 part in 1000 in one of these would make about 5 per cent. difference in the calculated value of z. Provided sufficient data are available, it is more satisfactory therefore to use an average value of z*. Besides improving the accuracy of the results, this also halves the number of the necessary observations, as there is then only one unknown in equation (6), so that one flow suffices to obtain a result.

§ 7. MEASUREMENT OF SPECIFIC HEAT BY THE METHOD

Although primarily designed for the measurement of the total heat, the apparatus has been used to measure specific heat. The knowledge of the total heat H_2 at the outflow temperature may be obtained with the mixture apparatus itself by means of a series of preliminary determinations of the mean specific heat over comparatively short ranges of temperature, say 20°–30° C.

---

* Cf. H. L. Callendar and J. H. Brinkworth, *Phil. Trans.* A, **215**, 391 (1915).

S If S is the mean specific heat of the oil, then

$$(H_1 - H_2)\, m = S(t_1 - t_2)\, m = sd\theta M + zd\theta \qquad \text{......(7)},$$

B or if

$$B = sd\theta M/(t_1 - t_2)\, m,$$

$$S = B + zd\theta/(t_1 - t_2)\, m \qquad \text{......(8)}.$$

If, as before, the experiment is arranged so that the same temperature-rise is used with different rates of flow, and if the inflow temperature of the oil is kept the same, then the outflow temperature cannot be quite the same. As a result the mean temperature of the oil is changed, and since S in equation (8) is no longer constant it is impossible to eliminate the heat-loss between two such equations in the usual way. In cases where the value of z is known from previous experiments it may be considered as a constant of the apparatus, as was explained above, and in this way an immediate solution of the difficulty is provided. When this is not so, the difficulty may be overcome in two ways. First, if the difference of mean temperature is small the values of B may be corrected to the same temperature by the assumption of an approximate value for the rate of change of specific heat with temperature. In a second and more satisfactory method the inflow temperature of the oil is adjusted to keep the mean temperature the same for the different flow-rates. This is rather a laborious process since the outflow temperature is partly dependent on the inflow temperature, and partly on the temperature-rise of the water stream. After a little experience, however, it is possible to estimate the required values fairly closely. Now this change of conditions may seriously affect the assumptions regarding the heat-loss, on which the equations are based. This was tested experimentally by plotting B, equation (8), against $d\theta/(t_1 - t_2)\, m$ and resulted in the conclusion that the assumptions were still justified to at least the order of accuracy of the observations. Actually it is the mean specific heat that is measured, but over this short range of temperature it may be supposed to be equal to the true specific heat at the mean temperature, i.e. the differential $(dH/dt)_p$ of the total heat at constant pressure. By integration, the values of the total heat H_2 at the outflow temperature are then calculated, for use in the main series of experiments at higher temperatures.

THE DETERMINATION OF THERMAL CONDUCTIVITY AND ITS TEMPERATURE-VARIATION FOR MEDIUM CONDUCTORS

By C. R. ENSOR, B.Sc., A.R.C.S.
Imperial College of Science and Technology

Received May 7, 1931.

ABSTRACT. A plate method for the determination of thermal conductivity and its variation with temperature between 0 and 100° C. is described. Although specially adapted for medium conductors (of the order 0·001 to 0·02 c.g.s. units) such as rocks, it can be used for substances of lower conductivity.

§ 1. INTRODUCTION

In previous determinations of the thermal conductivities of poor or medium conductors by direct steady-state methods it has been customary to use specimens in the form of either a spherical shell, a hollow cylinder, or a plate or slab. While methods involving the use of a spherical shell or a cylinder possess certain advantages, yet on account of the ease with which specimens in the form of rectangular plates can be prepared and of the simplicity of construction of the necessary apparatus, the plate method has found most favour. It is with this method that the present paper deals.

If heat be supplied to one of the large faces of a rectangular plate at a constant rate, the determination of the thermal conductivity of the material of the plate involves the accurate measurement of two quantities, namely the heat-flow per unit area across the plate and the temperature-gradient normal to the surface to which heat is supplied. The rate at which energy is supplied can be measured with great accuracy when electrical heating is adopted, the chief difficulty being the estimation of the heat which is lost by conduction and radiation from the sides of the plate; this loss should therefore be reduced to a minimum or eliminated altogether. The losses can be made very small by using very thin plates*, a procedure which is satisfactory with poor conductors but becomes impracticable with medium conductors such as rocks owing to the small temperature-gradient. A thickness of at least 1 cm. is desirable, particularly if the specimen is not homogeneous for in that case a thin plate would not be a representative specimen. Thus by using thick plates increased accuracy in the measurement of temperature-gradient is secured at the expense of a greater lateral heat-loss. Guard-ring methods† have been used to eliminate the lateral heat-loss, such methods being ideal theoretically though they involve a complication of apparatus which it is the aim of the present method to avoid. In the present investigation a method has been used by means of which the losses can be reduced to about 5 per cent. or less, even with thick specimens, the heat-loss or emissivity being determined by a subsidiary experiment with the same apparatus. Determinations of conductivities over the ranges 15 to 30° C. and 105 to 120° C. have been made for several substances, the values ranging from 0·002 to 0·014 c.g.s. units.

---

* Eg. E. Griffiths and G. W. C. Kaye, *Proc. R.S.* A, **104**, 71 (1923).

† E. Griffiths, "Heat Insulators," *Special Report No.* 35. *S.I.R.* (1929).

§ 2. DESCRIPTION OF APPARATUS

The system of plates in position in the constant-temperature enclosure is illustrated in figure 1. In order to ensure symmetry in the heat-flow two similar specimens were used, one on either side of the hot plate. The latter consisted of a unit made by sandwiching two nichrome-wire-asbestos heating mats, connected in parallel, between two brass plates each 15 cm. × 14 cm. × 1 cm. which are screwed together tightly. Each mat had a resistance of 100 ohms. Two mats in parallel were used for reasons of symmetry, their similar sides facing each other. The mats were insulated from the brass plates by sheets of mica and from each other by a wad of asbestos paper. On the outer faces of the specimens are mounted two similar channelled brass castings, each 15 cm. × 14 cm. × 1·5 cm., through which a rapid stream of water can circulate so as to carry away the heat transmitted through the specimens. These will be referred to as the cold plates.

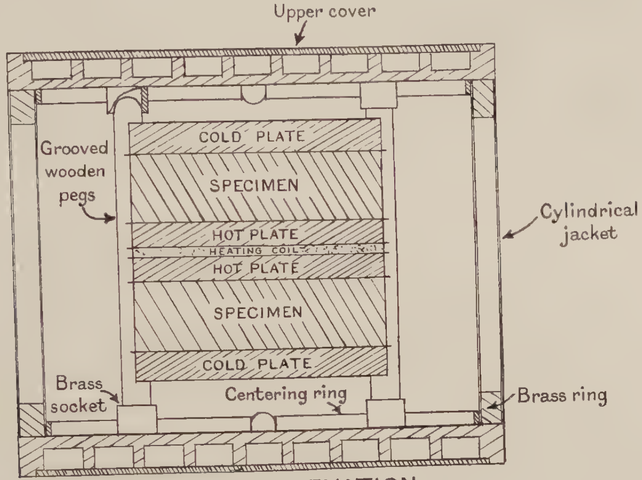
The temperatures of the cold faces of the specimens being in this way kept practically constant and equal to that of the enclosure, the mean excess temperature of the specimens is never allowed to become very high, whereas the heat-supply and consequently the temperature-gradient can be made quite large. Such a method, which can be called "calorimetric" (as distinct from an "emissivity" method, which differs in having no water-circulation through the cold plates and is similar in principle to the classical method of Lees*), has marked advantages in permitting large values of the energy supplied (say 50 to 100 watts) and of the temperature-gradient (say 5 to 20 degrees/cm.) and thus increasing the percentage accuracy with which these quantities can be measured. As the mean excess temperature of the specimens above that of the enclosure is very much less in the calorimetric method than in the emissivity method for the same heat-supply, the heat-loss (which is approximately proportional to the excess temperature) will also be very much less. The following figures, taken from tables 1 and 2, afford an excellent comparison of the two methods; it will be seen that the heat-loss from the sides of the specimens amounts to 31 per cent. of the heat generated in the heating coil in one case, but only 3 per cent. in the other.

	Emissivity method	Calorimetric method
Energy W supplied to coil	10·19	52·41 watts
Loss w_1 from sides of hot plate	1·44	1·40 ,,
Loss w_2 from sides of specimens	3·18	1·55 ,,
Mean flow $\overline{W}$ through specimens (i.e. $W - w_1 - w_2/2$)	7·16	50·23 ,,
Mean temperature θ_1 of hot face	25·70° C.	27·93° C.
Mean temperature θ_2 of cold face	23·61° C.	12·49° C.
Mean temperature drop $(\theta_1 - \theta_2)$	2·09° C.	15·44° C.
Thermal conductivity	$5·33 \times 10^{-3}$	$5·06 \times 10^{-3}$ c.g.s.

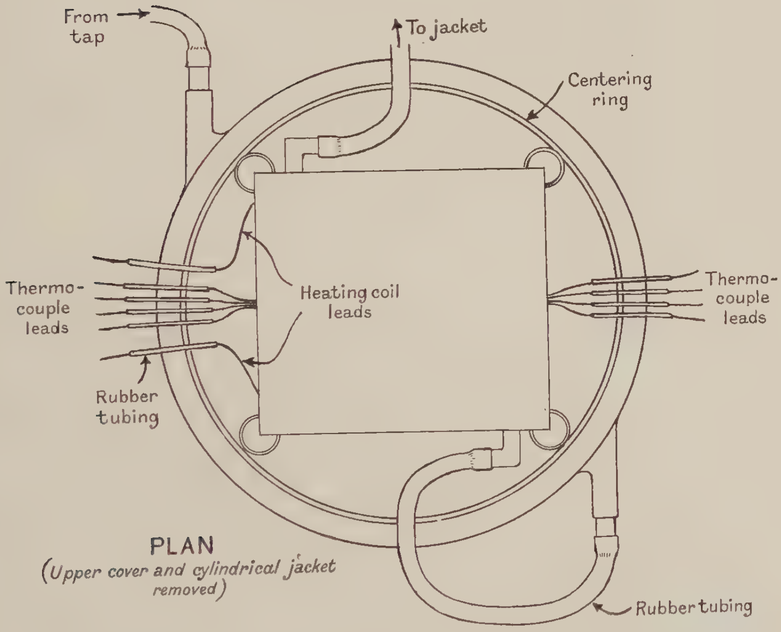
---

* *Phil. Trans.* A, **191**, 399 (1898).

An experiment performed without water-circulation through the cold plates gives the value of the emissivity which is used in calculating the heat-losses in the main (calorimetric) experiment. Since these losses are small, the emissivity is not required to a high order of accuracy, an error of 10 per cent. in its value producing an error of less than 0·5 per cent. in the value of the conductivity. It is rather surprising that the value of the conductivity deduced by the emissivity method should



SECTIONAL ELEVATION
(Rubber tubing and thermo-couples not shown)



PLAN
(Upper cover and cylindrical jacket removed)

Fig. 1.

differ by only 5 per cent. from the more reliable value given by the calorimetric method in spite of the smallness of the temperature-drop and the uncertainty in the value of the relatively large heat-loss in the former method. Assuming for the moment that no errors are introduced on this account, the discrepancy between the two values can only be explained by the fact that the usual assumption with regard to the effective heat-flow through the specimen is not justified. The assumption in $\overline{W}$ question is that the effective heat-flow $\overline{W}$ is the mean of the heat $(W - w_1)$ which enters the hot face and of that $(W - w_1 - w_2)$ which reaches the cold face, i.e.

$$\overline{W} = W - w_1 - w_2/2.$$

For example, if the effective flow is given by the expression

r

$$\overline{W} = W - w_1 - rw_2,$$

where $0 < r < 1$, the appropriate value of r which in the example quoted will make the values of the conductivity agree is 0·63, the values then becoming $5{\cdot}02 \times 10^{-3}$ and $5{\cdot}04 \times 10^{-3}$ respectively, the former being reduced by 6 per cent. and the latter by only 0·5 per cent. The difference between the values of the conductivity obtained by the two methods was always about 5 per cent. so that the error, if any, involved in taking the value of r as $\frac{1}{2}$ will only be 0·5 per cent. of the conductivity as deduced by the calorimetric method. In short, the experimental results lead one to suppose that the effective heat-flow should be given by

$$\overline{W} = W - w_1 - rw_2,$$

where $\frac{1}{3} < r < \frac{2}{3}$, the error in the conductivity due to the uncertainty in the correct value of r never exceeding 0·5 per cent.

The heating current is supplied by a battery of accumulators, the wattage being calculated from the resistance of the coil and the potential-difference between its terminals as measured with a calibrated voltmeter. The wattage can be measured in this way to the same order of accuracy as the other quantities, the necessity of using a more elaborate potentiometer method being thus dispensed with.

Measurement of temperature. It is important that the temperatures be measured at two points a known distance apart along the lines of heat-flow in the specimen. The practice of embedding thermocouples in the specimen itself is undesirable from the point of view of the inevitable distortion of the lines of heat-flow produced by the material used to cement the couples in place. It is also inadvisable to measure the temperatures of the hot and cold plates on the assumption that these give the temperatures of the specimen surfaces, particularly when the latter are hard or uneven, for then the thermal contact is poor and it is preferable to use thermocouples in direct contact with the surfaces, as pointed out by Griffiths*. The thermal contact can be improved by using between the surfaces a cementing material, the thickness of which should be very small in comparison with the thickness of the specimen, a condition difficult to fulfil with thin plates. With thick specimens (1 cm. or more) the accuracy of measurement of temperature-gradient is increased, and it is not necessary to adopt special methods of ensuring perfect plane parallelism of the faces or of measuring the thickness.

---

* *Loc. cit.*, p. 14.

In the present work the temperatures at the centres of the actual faces were measured by means of thermocouples in good thermal contact with the faces, the couples being in the form of very thin strips sandwiched between the specimens and the hot and cold plates. With brass plates of the thickness used here the temperature is uniform over the surface to within a short distance of the edges. The thermocouples were made by hard-soldering together 28-gauge copper and constantan wires and rolling them out to form a strip about 15 cm. long and 0·03 mm. thick, with the junction in the centre. Latterly constantan-manganin couples were used in preference to copper-constantan couples owing to the fragility of thin copper strip, the e.m.f. per degree being only slightly less. There is also the additional advantage that the temperature-coefficients of resistance of both constantan and manganin are small, so that the galvanometer deflection per microvolt has practically the same value at 0° C. as at 100° C. Readings of the e.m.f. were made with a slide-wire potentiometer adjusted to give a potential drop of 1 microvolt per mm. down the wire; the galvanometer, which was of the moving coil type, had a voltage-sensitivity of 2·5 divisions per microvolt. The e.m.f. could easily be measured to 1 microvolt, corresponding to a temperature of about 0·02° C. Subsequently the slide-wire potentiometer was replaced by a thermoelectric potentiometer of the Cambridge Scientific Instrument Co. The e.m.f./temperature relations were obtained experimentally with sample couples over the range 0° to 100°, one junction being in melting ice and the other in a vacuum flask containing water, the temperature of which could be controlled by a small heating coil and measured with a platinum resistance thermometer. If E represents the e.m.f. of the couple in microvolts for a hot-junction temperature of t° C. the parabolic equation

E

t

$$E = at + bt^2,$$

a, b

fits the observed values closely over the range 0° to 100° and can safely be extrapolated to 130°, the values of the constants being

$a = 38{\cdot}5,\quad b = 0{\cdot}0425$ for copper-constantan,

$a = 35{\cdot}6,\quad b = 0{\cdot}0412$ for constantan-manganin.

The e.m.f. for $t = 100$ is practically the same for all couples provided the latter be made from wire taken from the same two reels; in one case, for example, five constantan-manganin couples had the following e.m.f.'s: 3962, 3963, 3963, 3965 and 3967 microvolts. In calibrating the couples used in the apparatus it is therefore sufficiently accurate to determine the e.m.f.'s at 100° and apply a proportionate correction on the appropriate parabolic formula. It has been shown by Adams* that the relation for a copper-constantan couple over an extended temperature-range (0° to 350° C.) is accurately given by the formula

$$E = 74{\cdot}672t - 13892\,(1 - e^{-0{\cdot}00261t}).$$

---

* *J. Amer. Chem. Soc.* 36, 65 (1914).

Over the range of temperatures used in the present work (0°–130°) the simpler parabolic formula gives values of the e.m.f. which agree with those obtained from the above formula to within 2 or 3 microvolts.

The four thermocouples are insulated from the hot and cold plates by thin sheets of mica 0·05 mm. thick and of area slightly greater than that of either plate. These sheets must make good thermal contact with the hot and cold plates and with the surfaces of the specimens. A suitable substance for this purpose is British pitch, which is sufficiently fluid at 100° to flow over the surface and sufficiently viscous to be retained between the plates at 130°, the highest temperature reached. The four mica sheets are first attached to the surfaces of the hot and cold plates by means of the pitch, layers of pitch are then formed on the surfaces of the mica sheets; and the whole system of plates, including the two specimens with the thermo-junctions in place, is mounted in a framework to prevent slipping. Steam is now circulated through the cold plates, and under the pressure of a 28-lb. weight the surplus pitch is gradually squeezed out until very thin layers exist between the surfaces. Owing to the high viscosity of pitch even at 100° this may take a considerable time, but it is inadvisable to expedite matters owing to the danger of creating small air pockets in the layers of pitch.

The constant-temperature enclosure. In order to make the external conditions definite, and to investigate the thermal conductivity above 100° C., the apparatus must be placed in a constant-temperature enclosure. The latter consists of three portions, a hollow cylindrical jacket through which water or steam may circulate, and an upper and a lower cover channelled for water- or steam-circulation in the same way as the cold plates of the apparatus. Through the lower of the brass rings which form the ends of the cylindrical jacket are bored four small holes on either side for the passage of the thermocouple and heating-coil leads, and two $\frac{3}{8}$-in. holes, one on either side, for the passage of rubber tubing carrying the water circulating through the lower cold plate. A similar pair of holes through the brass ring at the upper end of the cylindrical jacket suffices for the rubber tubing connected to the upper cold plate. On the inner surface of the lower cover are soldered four brass sockets, the centres of which are at the corners of a rectangle of the same size, 15 cm. × 14 cm., as the faces of the system of plates. Four $\frac{3}{8}$-in. wooden rods are fixed in these sockets, the rods being grooved along their length to within an inch of their base so as to support the system of plates at the corners, thus preventing any sliding of one plate over another.

§ 3. EXPERIMENTAL PROCEDURE

In carrying out a determination at room temperature, a rapid stream of water from the tap is passed through the lower cover, lower cold plate, cylindrical jacket, upper cold plate and upper cover in the order named. The heating current is then established and after the lapse of an hour the e.m.f.'s of the four thermocouples are measured until constant values are indicated. Temperature-readings are obtained in this way for different values of the potential-difference between the heating coil terminals. The stream of water is sufficiently rapid to give, for a supply of 100 watts to the heating coil, a rise of temperature of not more than 0·4° C. in passing through the cold plate, this rise of temperature being observed by means of mercury thermometers inserted in the circulating medium just before and after passage through one of the cold plates. A series of temperature-readings having been obtained for different values of the heating current, a series of emissivity readings is made over the same temperature-range by disconnecting the rubber tubing from the cold plates, the water-flow being through the jacket and covers only. Much smaller values of the heating current suffice in this case, but the realization of steady conditions is prolonged to about 8 to 10 hours, instead of one hour as in the calorimetric method.

The procedure was similar in making determinations of the conductivity above 100° C., except that steam was passed through the system in the reverse order, i.e. downwards instead of upwards, any tendency to superheat being thus avoided; the steam was then condensed and returned to the boiler.

§4. THEORY OF THE METHOD

Determination of the emissivity. Let

W be the energy supplied to heating coil in watts; W
d_h the thickness of the hot plate in cm.; d_h
d_c the thickness of each cold plate in cm.; d_c
d_s the mean thickness of the specimen in cm.; d_s
p the perimeter of the specimen in cm.; p
A the area of face of the specimen in cm.^{2}; A
θ_1 the mean temperature of the hot faces in degrees C.; θ_1
θ_2 the mean temperature of the cold faces in degrees C.; θ_2
ϕ the temperature of the enclosure in degrees C.; ϕ
h the emissivity in watts/cm.^{2}-degrees; and h
K the thermal conductivity in c.g.s. units. K

Then it follows that in the steady state

$$W = h\left\{pd_h(\theta_1 - \phi) + 2pd_s\left(\frac{\theta_1 + \theta_2}{2} - \phi\right) + 2(pd_c + A)(\theta_2 - \phi)\right\},$$

from which the value of h at a mean temperature of $(\theta_1 + \theta_2)/2$ can be determined. The assumption is here made that h is the same for all the surfaces and is independent of the temperature. As the difference between θ_1 and θ_2 is never more than 3 or 4 degrees in this experiment the latter assumption is justified. The first assumption is not strictly legitimate even if the different surfaces be made similar by varnishing, so that the above equation gives only a rough average value for the emissivity. As was pointed out previously, however, a comparatively large error on this account influences the value of the conductivity to only a small extent.

K The approximate value of the conductivity K as given by this method is

$$K = \overline{W} d_s / 2A\,(\theta_1 - \theta_2) \times 4{\cdot}18,$$

$\overline{W}$ where $\overline{W}$, the effective flow through the specimens, is given by

$$\overline{W} = W - hpd_h\,(\theta_1 - \phi) - hpd_s\{(\theta_1 + \theta_2)/2 - \phi\}.$$

Determination of the thermal conductivity by the calorimetric experiment. If, as before, θ_1 and θ_2 represent the mean temperatures of the hot and cold faces respectively in the calorimetric experiment, the hot plate will be at an excess temperature of $(\theta_1 - \theta_2)$ above that of the enclosure, and the specimens will be at an excess temperature of $(\theta_1 - \theta_2)/2$ approximately, since the temperatures of the cold faces and of the enclosure are practically the same.

The effective flow is therefore given by

$$\overline{W} = W - h_1 pd_h\,(\theta_1 - \theta_2) - h_2 pd_s\,(\theta_1 - \theta_2)/2,$$

h_1, h_2 where h_1 is the emissivity at a temperature θ_1, and h_2 is the emissivity at a temperature $(\theta_1 + \theta_2)/2$, these values being given by the emissivity experiment.

The thermal conductivity is, as before, given by

$$K = \overline{W} d_s / 2A\,(\theta_1 - \theta_2) \times 4{\cdot}18,$$

at a mean temperature $(\theta_1 + \theta_2)/2$.

§ 5. SPECIMEN OF OBSERVATIONS

As an example of the method the observations are given in some detail for slate

$$\begin{aligned} d_h &= 2{\cdot}35 \text{ cm.}, \\ d_c &= 1{\cdot}565 \text{ cm.}, \\ d_s &= 2{\cdot}795 \text{ cm.}, \\ p &= 58{\cdot}7 \text{ cm.}, \\ A &= 215{\cdot}0 \text{ cm.}^2. \end{aligned}$$

Table 1. Values of the emissivity.

W (watts)	θ_1 (° C.)	θ_2 (° C.)	ϕ (° C.)	$(\theta_1 + \theta_2)/2$ (° C.)	h (watts/cm.^{2}-degree)
5·73	19·31	18·19	9·85	18·75	$6{\cdot}15 \times 10^{-4}$
6·98	21·88	20·52	10·50	21·20	$6{\cdot}23 \times 10^{-4}$
8·94	24·21	22·49	10·25	23·35	$6{\cdot}53 \times 10^{-4}$
10·19	25·70	23·61	9·55	24·65	$6{\cdot}47 \times 10^{-4}$
11·91	28·45	25·97	9·90	27·21	$6{\cdot}60 \times 10^{-4}$
14·78	32·33	29·24	10·05	30·79	$6{\cdot}84 \times 10^{-4}$

Values obtained above 100° C. ranged from $9{\cdot}34 \times 10^{-4}$ at a mean temperature of 108·62° C. to $10{\cdot}72 \times 10^{-4}$ at a mean temperature of 127·51° C. By plotting emissivity against mean temperature graphs are obtained from which the appropriate value of h can be read off in deducing the losses in the main experiment.

Table 2. Values of the thermal conductivity.

W (watts)	θ_1 (° C.)	$(\theta_1 - \theta_2)$ (° C.)	w_1 (watts)	w_2 (watts)	$\overline{W}$ (watts)	$(\theta_1 + \theta_2)/2$ (° C.)	$K \times 10^3$ (c.g.s.)
32·87	22·76	9·71	0·85	0·96	31·54	17·90	5·052
35·63	23·20	10·49	0·92	1·04	34·19	17·96	5·067
47·95	27·53	14·02	1·27	1·41	45·97	20·52	5·100
52·41	27·93	15·44	1·40	1·55	50·23	20·21	5·060
63·16	31·52	18·62	1·74	1·92	60·46	23·21	5·049
69·76	33·22	20·47	1·94	2·12	66·76	23·23	5·072
74·54	35·32	21·92	2·10	2·28	71·30	24·36	5·057
80·46	37·13	23·64	2·31	2·48	76·91	25·31	5·059
93·89	41·00	27·53	2·76	2·93	89·66	27·23	5·064
104·0	44·33	30·51	3·14	3·28	99·22	29·07	5·058
109·2	46·00	32·12	3·43	3·50	104·0	29·94	5·035
115·7	47·99	33·98	3·60	3·74	110·2	31·00	5·044

The following values of $K \times 10^3$ were obtained for mean temperatures ranging from 105·43° C. to 113·88° C., the values of W ranging from 28·15 watts to 73·96 watts, and $(\theta_1 - \theta_2)$ from 8·76° C. to 22·82° C.:

4·694, 4·684, 4·697, 4·690, 4·694, 4·670, 4·679, 4·672, 4·681, 4·702, 4·671, 4·690.

The above values of the conductivity are plotted against the mean temperature in figure 2.

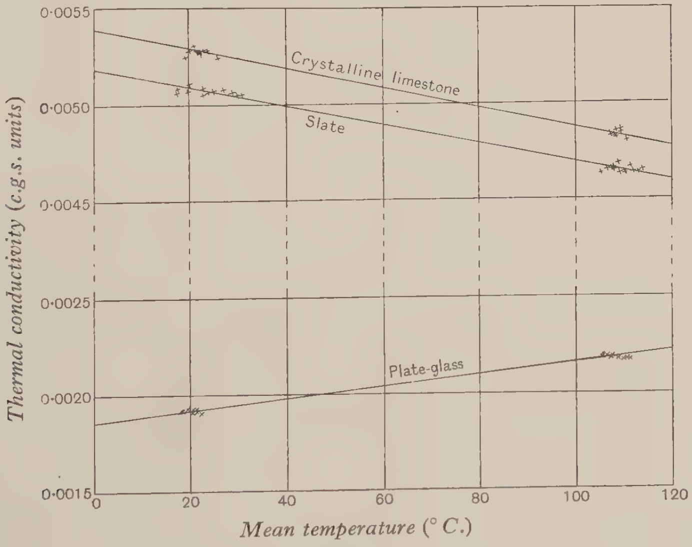


Fig. 2.

On the assumption that a linear relation

$$K_\theta = K_0 (1 + \alpha\theta),$$

K_θ, K_0, α

holds over the range 0° C. to 130° C. the following values are obtained:

$$K_0 = 0{\cdot}00517 \text{ c.g.s. units,}$$

$$\alpha = -0{\cdot}00085.$$

It will be noted that for this specimen the lateral loss amounts to 3·4 per cent. of the total heat supplied at room temperature. At 100° C. the loss is nearly 5 per cent. By cutting down the plates to a thickness of ¼ in. it would be possible to reduce the lateral loss to 1 per cent., while still maintaining an accurately measurable temperature-difference. In spite of the comparatively large heat-loss the values obtained show a fair consistency, as will be seen from the table; the consistency is even greater in the case of plate glass, for which, owing to its small thickness (¼ in.), the percentage loss is less. It may be remarked that the determinations at steam temperatures were generally more erratic than those at room temperature.

§6. SUMMARY OF RESULTS

The following substances were investigated: plate glass, slate, crystalline limestone and quartzite. The quartzite was obtained from South Africa; the sources of the limestone and the slate are not known. The specimens of slate show evidence of laminations in planes parallel to the largest faces (i.e. at right angles to the direction of heat-flow).

The values of the thermal conductivity at 0° C. and the temperature-coefficient are given in table 3.

Table 3.

Substance	Density (gm./cm.^{3})	K_0 (c.g.s.)	α
Plate glass	2·55	0·001845	+ 0·00168
Slate	2·78	0·00517	− 0·00085
Crystalline limestone	2·70	0·00539	− 0·00095
Quartzite	2·95	0·01493	− 0·00163

Except in the case of plate glass, values obtained by other investigators vary considerably. These variations are undoubtedly due in part to differences in the composition of substances of the same name which may have been quarried from widely separated localities.

For plate glass Meyer* obtained the value 0·00179 at 12·5° C., while the value given by Niven and Geddes† (0·001923 at 20° C.) agrees with the author's.

Previous values for slate are considerably lower than the above value; Lees and Chorlton‡ give 0·00357 at 94° C. while Herschel, Lebedour and Dunn§ obtained a value of 0·0034 perpendicular to the cleavage planes, the value in a direction at right angles being much higher. The low values could be explained if the specimens of slate used by these observers were more markedly laminar than those used in the present work.

---

* *Wied. Ann.* **34**, 596 (1888).

† *Proc. R.S.* A, **87**, 535 (1912).

‡ *Phil. Mag.* **41**, 495 (1896).

§ *Brit. Ass. Report*, **49**, 58 (1879).

Limestones and marbles vary considerably, as judged by the wide range of values of conductivity; Poole* gives values ranging from 0·0046 to 0·0057 at 40° C. and 0·0039 to 0·0049 at 100° C., those at the lower temperature being in substantial agreement with the determinations of Herschel, Lebedour and Dunn†. Values as high as 0·007‡ have been obtained for marble.

The comparatively small number of determinations of temperature-coefficients shows even greater discrepancies between the values obtained by different observers. According to the present work slate, limestone and quartzite possess negative coefficients, and this result is in agreement with those obtained for the majority of rocks. In connexion with the positive value obtained for plate glass it may be noted that Lees§ gives a value of + 0·0025 for window glass.

§ 7. ACKNOWLEDGMENT

The above investigation was suggested by the late Prof. H. L. Callendar, F.R.S., from whose constant interest and advice the author derived much valuable help, which he gratefully acknowledges.

---

* *Phil. Mag.* **24**, 45 (1912).

† *Loc. cit.*

‡ A. Eucken, *Ann. d. Phys.* **34**, 185 (1911).

§ *Loc. cit.*

THE ATTENUATION OF ULTRA-SHORT RADIO WAVES DUE TO THE RESISTANCE OF THE EARTH

By R. L. SMITH-ROSE, D.Sc., Ph.D., A.M.I.E.E.
and J. S. McPETRIE, B.Sc.
Wireless Division, National Physical Laboratory

Received March 3, 1931. *Read June* 5, 1931.

ABSTRACT. This paper describes an investigation of the attenuation of radio waves, of wave-lengths between 5 and 10 metres, when transmitted directly along the earth's surface. A brief description is given of the transmitters employed, one being a fixed installation used with an input power supply of the order of 500 watts, the other a transportable set operated with an input supply of about 50 watts obtained from batteries.

The observations of field-intensity were obtained by measurement of the audio-frequency voltage across the telephones of a simple two-valve loop receiver, a brief description of which is given. Measurements were carried out at both Slough and Teddington of the field-intensity at various distances from the transmitter up to 700 metres. In some of the experiments a negative attenuation effect was observed in the radiated field over a distance of about 4 wave-lengths. Later measurements carried out under more favourable conditions did not show this effect, which was, therefore, attributed to the interference of waves reflected from trees and buildings in the neighbourhood of the transmitter. Some qualitative observations were made at distances up to 20 miles with a single-loop direction-finder. These observations showed that the signal intensity on such short wave-lengths depends to a great extent upon the existence of obstacles in the path of transmission. The signal-intensity at a distance of 20 miles over a direct air line was of the same order as that obtained at 4 miles for transmission along the ground.

A comparison has been made between the experimental results and those calculated from a simple wave-attenuation theory, the electrical constants of the earth being taken into account. As a result of this comparison, the value of the conductivity of the earth appears to lie between 5×10^8 and 30×10^8 e.s.u. for the frequencies of 30 to 60 megacycles per second employed. These values correspond to resistivities of from 1800 to 300 ohm/cm.^{3} The most suitable value of the dielectric constant of the earth is about 10, although the experimental method does not enable this to be obtained with any great accuracy.

A brief description of some experiments carried out with a single-loop direction-finder on the wave-lengths under consideration is appended to the paper.

§ 1. INTRODUCTORY

During the past few years considerable progress has been made in the technique of radio transmission and reception on ultra-short wave-lengths (below 10 metres), although such wave-lengths have scarcely yet been applied to practical communication. While radio transmission to long distances depends upon the propagation-facilities provided by the upper regions of the atmosphere, transmission over the earth's surface depends rather upon the scattering and absorption-effect of obstacles on or near the earth's surface, and upon the absorption of energy in the earth. On the first point it is easily understood that such objects as buildings, hills, trees, etc., whose dimensions are negligible compared with the longer wave-lengths, may become serious obstacles in the path of ultra-short waves whose wave-length is comparable with or smaller than the principal dimensions of the obstacles. On the matter of the attenuation of radio waves due to the finite conductivity of the earth, a certain amount of data has been made available during the past few years as a result of experiments carried out on longer wave-lengths (1, 2, 3, 4, 5, 6). These data have been used on the one hand to compare the experimental results with the various theoretical formulae which have been suggested to account for the effect of the earth's resistance, and on the other hand to deduce values for the conductivity and dielectric constant of the earth. Even were complete agreement reached on the theoretical side it would still be desirable to ascertain to what extent these electrical constants of the earth vary with the frequency of the oscillations employed.

The objects of the investigations described in the present paper were, firstly, to extend the existing data on ground-wave attenuation into the region of wave-lengths below 10 metres (frequencies above 30 megacycles/sec.), and secondly, to endeavour to deduce values for the electrical constants of the earth at such frequencies.

§ 2. DESCRIPTION OF TRANSMITTERS

The experimental portion of the work was carried out partly at the Radio Research Station, Slough, and partly at the National Physical Laboratory, Teddington. A description of the principles underlying the design of the transmitters employed has been given in a former publication (7): which contained illustrations of the equipment installed at Slough. At this station the transmitter comprised a push-pull oscillator using two 250-watt valves feeding a single tuned oscillatory circuit, the arrangement being as shown in the schematic diagram in figure 1. The

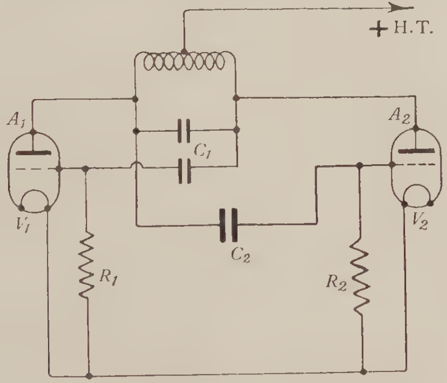


Fig. 1. Schematic circuit diagram of two-valve push-pull transmitter.

valves were erected on a skeleton wooden panel, and were so arranged that the connexions from the valve electrodes to the tuned circuit were as short as possible. Suitable choke-coils were inserted in the leads to filament and anode, in order to restrict the oscillatory current as far as possible to the tuned circuit. The valve filaments were operated from a 16-volt battery and the anode current was obtained from a motor-generator giving a d.c. supply at from 2000 to 5000 volts. When operating with an input supply of a few hundred watts to the set the circulating current in the tuned circuit was several amperes at wave-lengths between 5 and 10 metres, this range of wave-length being obtained by the use of different sizes of single-turn inductance loops. In some of the experiments the radiation direct from this loop was adequate for measurement purposes, and the arrangement possessed the advantage of forming practically a point source. For other measurements at greater distances, however, the loop was coupled to a Lecher-wire system by means of which the radio-frequency energy could be supplied to a half-wave aerial erected at some 10 metres from the transmitting hut. When both the Lecher-wire system and the aerial were accurately tuned to the working wave-length, the current at the centre of the aerial was of the order of 0·5 amp. The aerial was constructed in a telescopic form so that it could easily be adjusted to resonate at the desired wave-length.

In addition to this installation a smaller transmitter was constructed. This employed an essentially similar circuit arrangement, but used two 25-watt valves of a type which could be operated from a 300-volt anode-current supply. For this purpose the set could be operated from a 12-volt battery, a small motor-generator being used for obtaining the anode current, or alternatively the set could be operated from a 6-volt filament battery and a 300-volt h.t. battery. The latter method was found to be preferable as it avoided the necessity of a smoothing circuit in the h.t. supply, and gave greater constancy of frequency of the generated oscillations. The transmitter, with the exception of the inductance loop of the oscillatory circuit, was built into a screened box which was mounted on a table, which carried the batteries and was provided with castors. The whole set was thus transportable as a unit, and could be placed on any suitable site with no difficulty arising from interference due to power-supply cables. Since the main portion of the transmitter was screened and radio-frequency currents were excluded from the battery-supply leads by the use of suitable choke coils and condensers, the inductance loop formed practically a point source of radiation, the strength of which was found to be adequate for the experiments for which this transmitter was used.

§3. DESCRIPTION OF RECEIVER AND METHOD OF MAKING MEASUREMENTS

The type of receiver employed has been described in the publication to which reference has already been made(7). It comprised a single-valve retroactive detector stage followed by one stage of audio-frequency amplification, the schematic circuit diagram being given in figure 2. A single-turn loop was used as the receiving aerial and as the inductance of the sole oscillatory circuit employed. This loop was mounted directly on the top of a screened box which contained the whole of the rest of the receiver including the batteries. By the use of single-turn loops of diameters between 5 and 12 in., constructed of $\frac{1}{8}$ in. copper tube, wave-lengths from 4·8 to 10·8 metres could be covered.

The output from this receiver was measured by connexion of a suitable valve-voltmeter directly across the output terminals, a measure of the audio-frequency voltage across the telephones being thus given. In some of the experiments the radio-frequency current at the transmitter was modulated at a constant audio-frequency and no difficulties arose from note variation: in the majority of the experiments, however, continuous waves were used, and the signal current was reduced to an audible frequency by the autodyne method, the detector stage of the receiver being made to oscillate. Although a certain amount of difficulty was experienced due to note variation under these conditions, it was found that in favourable circumstances the beat frequency could be maintained constant long enough for a measurement to be made, and that the readings could be repeated to a reasonable degree of accuracy. This was especially the case with the battery-driven transmitter with which the difficulties due to frequency variation were relatively small.

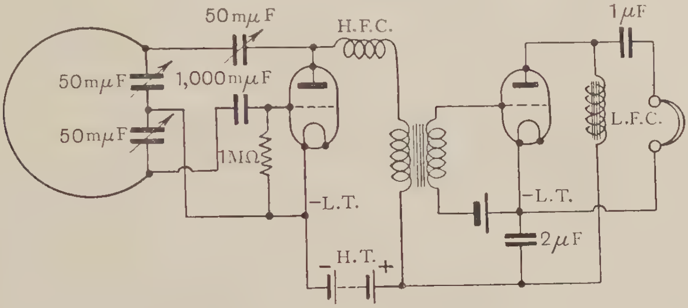


Fig. 2. Two-valve short-wave loop receiver for field-strength measurements and direction-finding (wave-length range 4 to 10 metres).

The receiver used in this way for relative signal-intensity measurements was calibrated directly from the transmitter by variation of the oscillatory current while measurements of the signal output were made with the receiver at a fixed position. In this way it was determined that up to outputs of nearly two volts, the measured output was proportional to field-intensity. Three ranges were provided on the valve-voltmeter, and the sensitivity of the receiver could be altered by variation of the retroaction adjustment, but care was taken not to use too critical a value of this, so that small accidental variations would not produce an appreciable effect.

The procedure adopted in obtaining attenuation curves was first to mark out the line of propagation required with wooden pegs at intervals of 10 metres or 100 metres from the transmitter. The receiver was then taken in succession to each position and a measurement of the output made for each of two or three values of transmitter current. No alteration of receiver conditions was made in changing from one position to the next, and the transmitting-aerial current was measured throughout the experiments by means of a thermo-ammeter inserted at its mid-point. During the measurements the receiver was placed directly on the ground and the observer lay alongside it to avoid any variable effects due to his presence, since in the upright position a man can produce quite a marked variation in the field-strength in his proximity on these short wave-lengths. In each experiment measurements were made in the above manner at each position over the full length of the run and were then repeated during the return journey to obtain a check. The readings were then reduced to a unit value of transmitting aerial current and also to the relative intensity at some position arbitrarily chosen for the purpose of the tests.

§4. EXPERIMENTAL PROCEDURE AND RESULTS OBTAINED

(*a*) *Measurements at Slough at short distances.* The short-wave transmitting hut at Slough was erected near a corner of a field which was bounded by a moat and a bank of trees. The trees were at a distance of from 50 to 100 metres from the hut, and there were two buildings at distances of from 25 to 50 metres. Over an arc of some 30° from the transmitting hut, however, there was a clear path which extended to a distance of over 600 metres and was free from trees, buildings, or other obstacles. The transmitting aerial was erected at a distance of 10 metres from the hut and was connected to the oscillator by a Lecher-wire system. The line of the Lecher wires was arranged along one side of the clear arc just referred to, and for the purpose of the measurements to be described below this line was taken as the zero direction.

In order to ascertain the effect of the various obstacles surrounding the transmitting hut, measurements were made of the field-intensity in various directions at distances varying from 7 to 100 metres, all conditions at the transmitter being maintained constant. At distances up to 18 metres the radiation-distribution was found to be fairly uniform in all directions around the transmitter, except where the hut was between transmitter and receiver. At a radius of 100 metres, however, the distribution of radiation varied greatly with the direction of transmission: the results obtained on the three wave-lengths employed are shown plotted in rectangular co-ordinate form in figure 3. The positions at which the circle of reception crossed the surrounding trees and the electric power cable supplying the transmitter are indicated in this diagram. It is clear from these graphs that while within the open sector of 0° to 30° mentioned above the field-intensity is reasonably constant for each wave-length, erratic variations in field-intensity were experienced in other directions. There is a pronounced drop in intensity, for instance, in the 120° direction where the receiving measurements were made beyond a belt of trees. In other directions the effect varies with the wave-length employed and indicates not only the absorption due to the trees but also the reflection and scattering effects which would be expected from obstacles several wave-lengths high. The power cable is seen to produce effects varying with the wave-length, the resultant intensity being due possibly to resonant phenomena in the cable itself. Since a vertical half-wave aerial was employed at the transmitter the radiation was polarized with the electric force in a vertical plane and it is, therefore, to be expected that trees, the lower portions of which are sensibly vertical, would form an effective screen to the passage of such waves. Further, it is reasonable to suppose that waves polarized with the electric force horizontal would penetrate the trees more easily, but their propagation along the ground itself would be very difficult. The investigation was concerned with propagation along the ground free from the effects of obstacles, and the use of horizontally polarized waves has not so far been investigated experimentally.

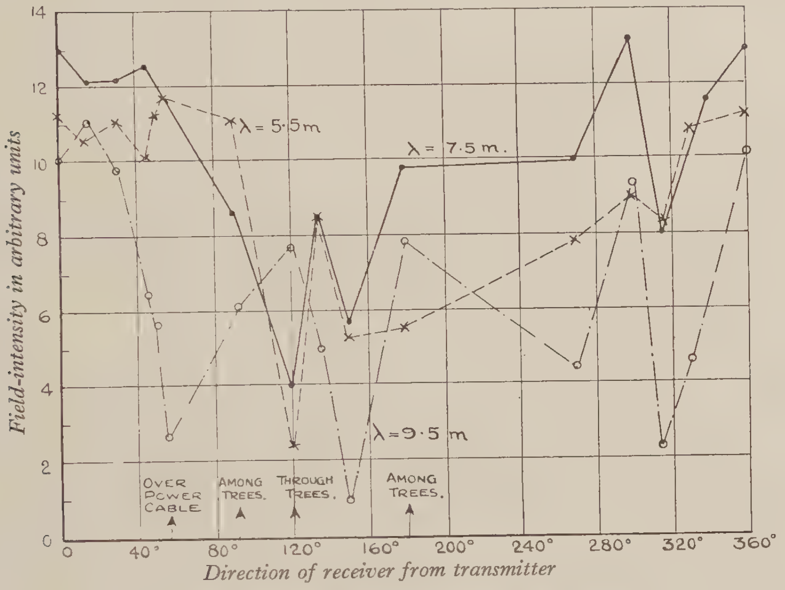
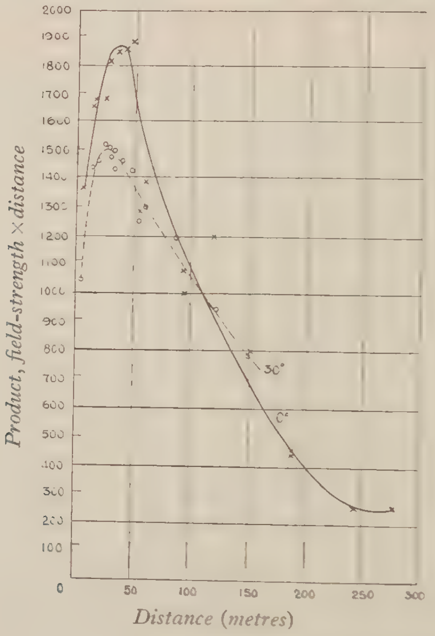


Fig. 3. Short-wave transmitter at Slough. Measurements of field-intensity in different directions at constant distance of 100 metres (wave-lengths 5·5, 7·5 and 9·5 metres).

Attention was now turned to the carrying out of field-intensity measurements at various distances from the transmitter in the clear sector. In the first series of tests the transmitting aerial was removed and the radiation direct from the loop of the oscillator used for measurements at distances of from 6 to 300 metres. Figure 4 shows the results of a series of such measurements made on a wave-length of 8·7 metres and in the two directions 30° apart which form the boundaries of the "clear" sector. The ordinates are given as the product of the field-intensity and distance for each position employed, and it may be pointed out that this quantity would be constant at all distances for the ideal case of propagation over a flat perfectly conducting earth. The graphs in figure 4 indicate that in each case, for short distances between transmitter and receiver, the product of field-intensity and distance *increases* with the distance, attaining a maximum value at a distance of about 36 metres. The suggestion has been made that this might be due to a mutual coupling effect between the transmitter and receiver tuned circuits, but this was considered to be unlikely since no difficulty was experienced in maintaining constant the conditions at the transmitter. It was next considered that the peak in the curve indicated a negative attenuation effect, as has been suggested by Ratcliffe(3, 5), to explain some of his own experimental results on wave-lengths of 1600 and 30 metres. Some doubt was felt about the validity of this explanation, however, because of the possible reflection effects which might occur from surrounding obstacles; and these doubts were confirmed by the fact that within the range under consideration the readings obtained with a direction-finder on the transmitter showed that large changes in the indicated bearing occurred with small changes in position. Furthermore, it may be recalled that in their experiments carried out in Bushey Park in 1905, Duddell and Taylor(8) found that the product of received current and distance from transmitter did not always decrease as the distance from the transmitter was increased, and in some cases a definite increase in the value of the product was recorded. These experiments were carried out on a wave-length of the order of 100 metres and these anomalous results were ascribed to scattering effects of the trees between transmitter and receiver. It was, therefore, decided to attempt the carrying out of more accurate measurements on a site free from the obstacles referred to above.



——×—— Direction from transmitter =0°.
– – –O– – – Direction from transmitter =30°.

Fig. 4. Field-strength measurements at distances of 6 to 300 metres from a small loop transmitter (wave-length 8·7 metres).

(*b*) *Measurements at Teddington at short distances.* For the purpose of these measurements a transportable type of transmitter was developed on the lines already described in § 2. The great advantage possessed by the use of this set was that it could be taken to a clear site and no difficulties due to the attachment of power-supply cables would arise. The next series of measurements was carried out on a field at the National Physical Laboratory approximately 250 metres square and clear of any obstacles. The transmitter was set up at a point at least 100 metres from any interfering obstacle along the boundaries of the field, so that a clear run 100 to 150 metres in length was obtainable before the receiver came under the influence of the conditions on the boundaries of the field.

As in the previous case, a measurement of the radiation in various directions from the transmitter was carried out. Since in this case the radiation was obtained entirely from the transmitting loop, this loop was turned for each measurement so that its plane was in the direction of the receiver. The results of measurements made in this way at a constant radius of 30 metres from the transmitter, and on the three wave-lengths of 5·5, 7·5 and 9·5 metres are shown by the graphs plotted in figure 5. Similar results were obtained at a radius of 50 metres in a check experiment made on a wave-length of 7·5 metres. From these graphs it is seen that within extreme limits of about ± 10 per cent. the radiation from the transmitter in the plane of the loop is uniform in all directions on each of the three wave-lengths employed. It was concluded, therefore, that the site in the neighbourhood of the transmitter was satisfactory, and that attenuation measurements might be made without risk of interference from the effects of external objects.

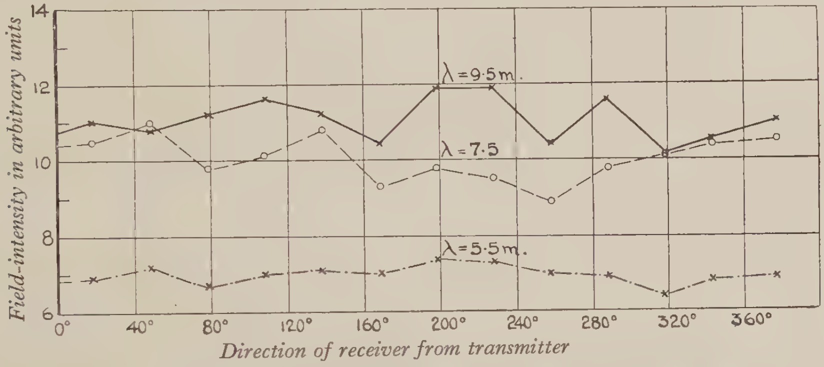


Fig. 5. Polar curves of portable transmitter at N.P.L., Teddington. Measurements of field intensity in different directions at constant distance of 30 metres (wave-lengths 5·5, 7·5 and 9·5 metres).

The results of a series of measurements carried out during a period of four days in July, 1930, are shown by the graphs plotted in figure 6 for the three wave-lengths employed. Measurements made on consecutive days under the same conditions on the same wave-length showed good agreement to within the experimental accuracy for observations on such short wave-lengths. This, as was previously stated, is of the order of 10 per cent. Further measurements made during a two-day period in

August, 1930, on the same site are shown in figure 7. These measurements were made with the direction of transmission reversed from that of the July experiments, by placing the transmitter at the opposite end of the site. A direct comparison test was made for the two directions of transmission on 27–28 August, 1930, and the results are shown by the two graphs plotted for a wave-length of 7·5 metres in figure 7. Within the limits of experimental error the two curves are in good agreement. This implies that the observed attenuation is independent of the direction of transmission and the results are, therefore, likely to be free from external interference conditions.

Viewing the curves in figures 6 and 7 as a whole, it is seen that there is no sign of the "negative-attenuation" effect previously observed in figure 4 at a distance of 30 to 40 metres from the transmitter, and it is likely that the peak in figure 4 is attributable to the interference of two sets of waves, one of which has reached the receiver after reflection from some object such as a building or a group of trees. In some of the measurements carried out under very dry conditions a slight rise in the curve was noticed at a distance of about 50 metres. On inspection of the site it was found that two strips of dried-up grass crossed the line of transmission at this point. These strips were subsequently found to mark out the directions of two disused tunnels at a depth of from 1 to 2 metres below the ground. As a result of the increased drainage conditions prevailing here, these strips of ground became very dry and produced a change in the ground conductivity, giving rise to interference effects which show up on the attenuation curves. After a period of wet weather both the

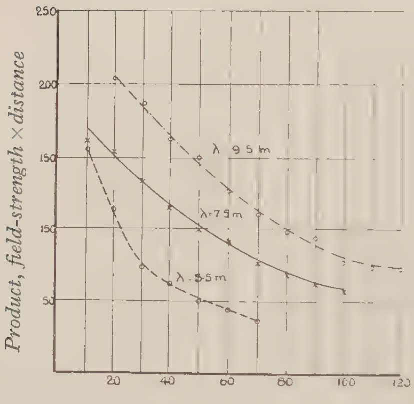


Fig. 6. Field-intensity measurements at distances up to 120 metres from a loop transmitter at the N.P.L., July 1930.

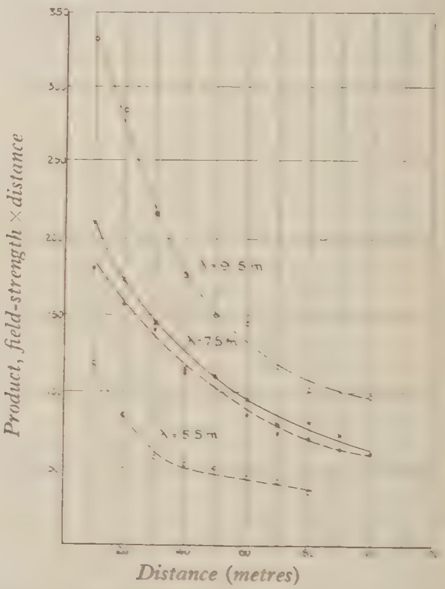


Fig. 7. Field-intensity measurements at distances up to 100 metres from a loop transmitter at the N.P.L., August 1930.

discoloration of the grass and the inflection of the curves disappeared. This is a result to be expected, since under normal conditions the surface layer of about 1 metre of soil is a sufficiently good conductor to screen the lower materials, unless these have a markedly superior conductivity.

(*c*) *Measurements from Slough at greater distances.* Some further experiments were carried out in an endeavour to obtain quantitative attenuation curves covering distances greater than the 120 metres to which the measurements given above were restricted. The site at Slough was chosen for this purpose since, as already stated, a clear path was available up to 600 or 700 metres in the most favourable direction. In these tests the transmitter was coupled to the vertical half-wave aerial, in which currents of from 0·1 to 0·5 amp. were employed. In order to avoid interference due to radiation from the transmitter itself the whole of the inside of the transmitting hut was screened with iron wire netting of half-inch mesh. This was found to be effective in reducing the radiation from the transmitter to an amount too small to be measured except at very short distances from the hut. The receiver was used in the same manner as previously, measurements of the signal output being made at each position for two or three values of transmitting aerial current.

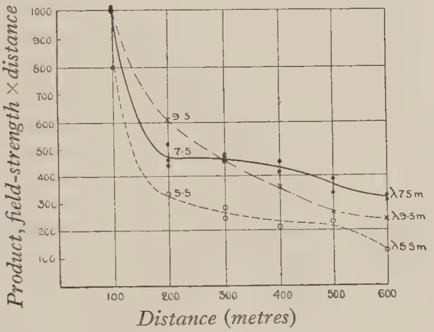
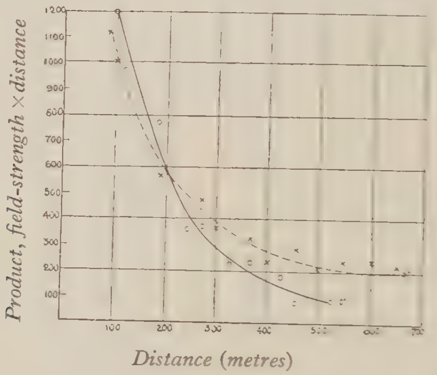


Fig. 8. Field-strength measurements at distances of 100 to 600 metres from a half-wave transmitting aerial (wave-lengths 5·5, 7·5 and 9·5 metres).

The results of a series of measurements made at distances of from 100 to 600 metres on the three wave-lengths of 5·5, 7·5 and 9·5 metres are shown in the graphs in figure 8. These measurements were taken for a direction of transmission 7° from the arbitrary zero direction defined above. The graphs show that while at first the attenuation increases as the wave-length is reduced, there is a marked change in the effect produced on the wave-length of 7·5 metres as compared with the other two wave-lengths. The fact that the curve for a wave-length of 7·5 metres crosses that for $\lambda = 9\cdot5$ metres at a distance of 300 metres from the transmitter indicates that the receiver is still under the influence of irregular propagation due to interference and reflection effects. Although at these positions the receiver was several hundred metres from the trees surrounding the site, it is evident that the effects were such as to increase the field intensity on the 7·5-metre wave-length as compared with that on 9·5 metres. Further tests showed that the field-intensity was not only dependent upon the wave-length, but also, to a fairly critical extent, upon the direction of transmission. For example, the results of two tests made upon the same wave-length of 7·9 metres for two directions 5° apart are shown in figure 9. All the measurements recorded in these graphs were taken with the receiver placed at a satisfactory distance from trees, huts, etc., and it is noteworthy that on the whole, the measured values for each set of conditions lie on a smooth curve.

Other measurements were made to ascertain the effect of an individual tree upon the field-intensity in its neighbourhood. As an example of the results obtained, it may be stated that at a distance of nearly 200 metres from the transmitter a movement of the receiver to 5 or 10 metres either side of the tree produced changes in field-strength of ± 50 per cent., so that in one position the field had three times the intensity obtaining in another position only 10 or 15 metres away.



——O—— Direction from transmitter =0°. ---×--- Direction from transmitter =5°.

Fig. 9. Field-strength measurements at distances of 100 to 700 metres from a half-wave transmitting aerial (wave-length 7·9 metres).

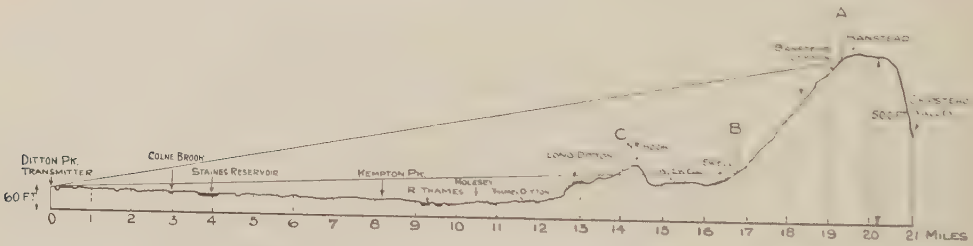


Fig. 10. Vertical section through path from R.R.S. Slough to Banstead.

For distances in excess of 700 metres it has been possible so far to make only qualitative experiments, the results of which are, however, very useful. At distances up to about 1 mile from the transmitter the received signal-intensity was adequate for taking readings on a direction-finder, although the accuracy of the bearings obtained varied in an erratic manner. At greater distances of from 4 to 7 miles over flat open country the signals were much weaker, but the d.f. bearings were more consistent and were accurate to 2° or 3°. At 8 miles the signals were only just definitely audible, and although many tests were made at this distance in various directions over the flat country, no position was found at which satisfactory reception was possible with the simple two-valve receiver employed. When, however, the receiver was taken to a point nearly 20 miles distant from the transmitter and at an elevation of over 500 ft., the signal-intensity was of the same order as that obtained at only 4 miles from the transmitter. This point is marked as A in the sectional contour of the path of transmission shown in figure 10, from which it can be seen that there is a clear optical path from A to the transmitter. As the receiver was brought towards the transmitter the signals became inaudible at the point B 17 miles distant, and at point C 14 miles from the transmitter the signals were audible but much weaker than at the more distant point A.

It is thus evident from such tests that even at distances of several miles the field intensity at a receiving point is to a great extent dependent upon the topography of the ground along the line of transmission.

§ 5. DISCUSSION OF RESULTS

The first deduction to be drawn from the experience gained in this investigation is that in order to make reliable measurements of the attenuation of ultra-short waves at short and medium distances it is necessary to have available a large expanse of flat open ground clear of all obstacles, both natural and artificial, particularly in the neighbourhood of the transmitter and receiver. It is not easy to obtain such a site more than a few hundred metres in extent. Although in the experiments described above the quantitative measurements have been limited to ranges of 600 or 700 metres, it is to be noted that this distance is of the order of 100 times the wave-length employed. The most satisfactory measurements were those made at Teddington and illustrated by the graphs in figures 6 and 7, and it was thought that these were sufficiently reliable to be compared with the theory of attenuation of electromagnetic waves transmitted along the ground.

In the second place figures 6 and 7 show no sign of the negative attenuation effect which is deducible from the theoretical work of B. Rolf (9), and which appears to have been confirmed by the experimental work of Ratcliffe (3, 5), already referred to.

The results of the present experiments would indicate, however, that it is possible that in Ratcliffe's experiments the phenomena under investigation were subject to disturbance by some spurious effect which could produce a result of the type illustrated in figure 4.

Next, any comparison of experiment with theory must be made on the basis of the substitution in the theoretical formula of various values of the conductivity and dielectric constant of the earth, in order to ascertain the theoretical conditions which best fit the practical results. A simple theory of the attenuation of electromagnetic waves has been worked out by J. S. McPetrie and will be described in detail in a later paper. From this theory it is shown that the reflection-coefficient at the earth is complex and is equal to

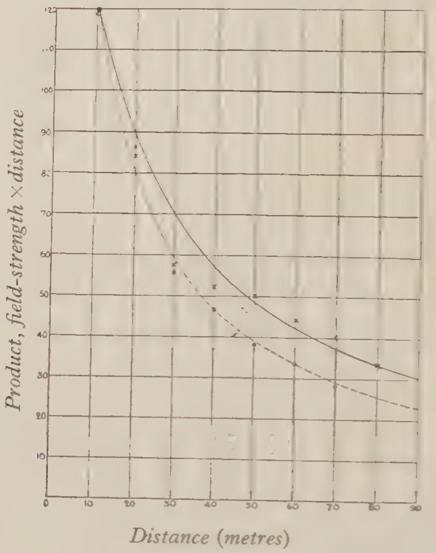
$$\frac{(k^2+4\sigma^2/f^2)\cos^2\theta-(c^2+d^2)-2j\cos\theta\,(2c\sigma/f+kd)}{(k^2+4\sigma^2/f^2)\cos^2\theta+(c^2+d^2)+2\cos\theta\,(kc-2d\sigma/f)},$$

θ, k, σ where θ is the angle of incidence on the earth, k and σ are respectively the dielectric
f constant and conductivity of the ground, f is the frequency of the incident wave,
c, d and c and d are determined by the relations

$$k-\sin^2\theta=c^2-d^2$$

and

$$\sigma/f=-cd.$$



Calculated curves: ——— $K=10$ $\sigma/n=40$, ------ $K=10$ $\sigma/n=10$.
Experimental results: • July 1930, Fig. 6. × Aug. 1930, Fig. 7.

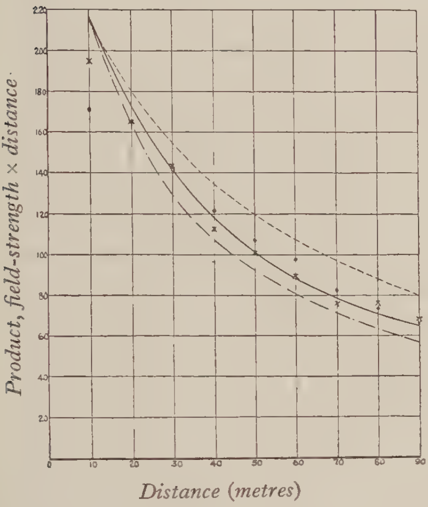
Fig. 11. Theoretical and experimental results obtained at N.P.L. (wave-length 5·5 metres).

K, K' If the reflection-coefficient be expressed in the convenient form $K-jK'$, the product of the field-intensity and distance from a simple vertical Hertzian dipole for the case in which both transmitter and receiver are near the earth's surface is proportional to

$$\sqrt{(1+K^2+K'^2+2K\cos\lambda-2K'\sin\lambda)},$$

λ in which λ represents the optical path difference between the ray direct from transmitter to receiver and that reflected by the earth's surface, and K and K' are the components of the complex reflection-coefficient for the angle of incidence which this indirect ray makes with the earth's surface.

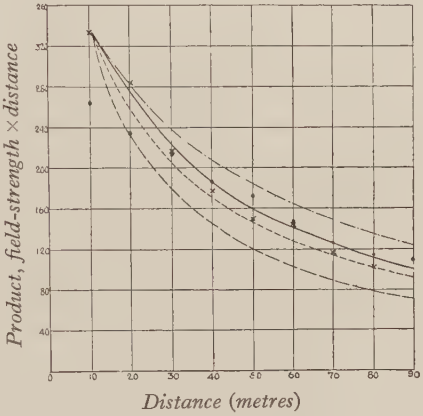
In figure 11 a comparison is made between the experimental results for a wave-length of 5·5 metres, as given in figures 6 and 7, and theoretical curves calculated from this formula for the following values in electrostatic units: $\sigma/f = 10$ and 40, $K = 10$. Similar graphs are given in figures 12 and 13 for the results obtained on wave-lengths of 7·5 and 9·5 metres. From these it will be seen that by a suitable choice of values of σ and K, satisfactory agreement can be obtained between theory and experiment. The nature of the variation of the theoretical curves for different values of σ/f is particularly shown in figure 13. Similar calculations have been made for different values of K between 5 and 80, but it was found that between these limits the value of K made little difference to the position of the theoretical curves. This result is partly to be expected from the fact that over the range required K is still smaller in value than the quantity $2\sigma/f$, with which it is associated in the theoretical formulae. In addition, if K is increased much beyond its assumed value of 10 the theoretical curve becomes too convex to the axes to fit the experimental results.



Calculated curves:
- - - - - - - $K = 10$ $\sigma/n = 200$.
——————— $K = 10$ $\sigma/n = 80$.
—•—•—• $K = 10$ $\sigma/n = 50$.

Experimental results:
• July 1930, Fig. 6.
× August 1930, Fig. 7.

Fig. 12. Theoretical curves and experimental results at N.P.L. (wave-length 7·5 metres).



Calculated curves:
—•—•—• $K = 10$ $\sigma/n = 200$.
——————— $K = 10$ $\sigma/n = 80$.
- - - - - - - $K = 10$ $\sigma/n = 60$.
— — — — $K = 10$ $\sigma/n = 25$.

Experimental results:
• July 1930, Fig. 6.
× August 1930, Fig. 7.

Fig. 13. Theoretical and experimental results obtained at N.P.L. (wave-length 9·5 metres).

A graphical comparison between theory and experiment carried out in this manner to values of σ and K for the observations made at the National Physical Laboratory in July and August, 1930 (figures 6 and 7). The results obtained from figures 11–13 are given in the following table.

Table showing the values of the conductivity (σ) of the earth as deduced from the experimental measurements of attenuation made at the N.P.L., Teddington, during July and August, 1930 (see figures 6 and 7).

The dielectric constant $K = 10$ throughout.

Wave-length (metres)	Frequency (mega-cycles/sec.)	Graphs in figure	For July		For August	
			σ/f	σ (e.s.u.)*	σ/f	σ (e.s.u.)*
				$\times 10^{8}$		$\times 10^{8}$
5·5	55	11	10	5·5	40	22
7·5	40	12	80	32	80	32
9·5	32	13	80	24	60	19

* A conductivity value of 10^{8} e.s.u. is equal to $1\cdot 1 \times 10^{-13}$ e.m.u. and corresponds to a resistivity of 9000 ohm/cm.^{3}.

It will be seen from this table that the values of σ vary between limits of $5\cdot 5 \times 10^{8}$ and 32×10^{8} e.s.u. for the three wave-lengths of 5·5, 7·5 and 9·5 metres (frequencies of 55, 40 and 32 megacycles/sec.). It is not considered that the variation with wave-length is significant in view of the experimental difficulties involved in measurements at such high frequencies; also there is no consistent difference in the results obtained in the two months of July and August. The above values of conductivity may be compared with those obtained on longer wave-lengths by previous workers. For example, on wave-lengths between 350 and 750 metres (frequencies between 860 and 400 kc./sec.) Smith-Rose and Barfield(1), using a tilting aerial method, obtained values of conductivity lying between $0\cdot 14 \times 10^{8}$ and $4\cdot 2 \times 10^{8}$ for the soil in different parts of the south of England; while in later investigations on attenuation Barfield(4) obtained values of from $0\cdot 2 \times 10^{8}$ to $1\cdot 0 \times 10^{8}$, the lower values of conductivity in this case being ascribable to the effects of trees. In their experiments on attenuation Ratcliffe and his co-workers(3, 5) have obtained values for σ of $0\cdot 5 \times 10^{8}$ for a wave-length of 1600 metres (frequency 190 kc./sec.); of $1\cdot 5 \times 10^{8}$ for a wave-length of 360 metres (830 kc./sec.); and $0\cdot 18 \times 10^{8}$ for a wave-length of 30 metres (10,000 kc./sec.). Thus the results of these investigators indicate that on wave-lengths between 30 and 1600 metres (frequencies from 10,000 to 190 kc./sec.) the conductivity of the earth lies between values of 0·14 and $4\cdot 2 \times 10^{8}$. It is difficult to assess the relative accuracy of the various methods of measurement employed, and it is therefore uncertain whether the variation in the values obtained is outside the overall limits of accuracy of the various experiments.

More recently M. J. O. Strutt(10) has experimented on the very short wave-length of 1·42 metres (210 megacycles/sec.) and has obtained a value of conductivity in excess of 10×10^{8} e.s.u. for soil which at lower frequencies possessed a normal value of about 1×10^{8}. This result, taken in conjunction with those reported in this paper, appears to indicate that there is a definite tendency for the apparent conductivity of the earth to rise appreciably at radio-frequencies in excess of 30 megacycles/sec.

It is hoped that with the aid of a more sensitive receiver the present experiments may be extended so that further quantitative data will be obtained for greater distances. Tests of various receivers suitable for use on ultra-short wave-lengths have been carried out recently, and the results suggest that the supersonic heterodyne type will be the most suitable for this purpose.

Also in order to deduce values of K for the earth with more accuracy, it will be necessary to extend the experimental measurements to still shorter wave-lengths. In this case it will probably be desirable to employ different methods of attacking the problem, for example, by raising the transmitter by a few wave-lengths above the ground and carrying out observations at short distances.

For the experimental results at longer distances already obtained, as illustrated in figures 8 and 9, it can be shown that the field-strength tends to decrease inversely as the square of the distance for distances in excess of 200 or 300 metres. This is a result which follows from the theory for transmission over uniform ground at distances of many wave-lengths from the transmitter, and it is suggested that this result is of direct importance in the application of very short waves to signalling purposes. When, however, either the transmitter or the receiver is elevated so that there is a direct optical-ray path between the two, and the propagation is independent of the effect of the earth, then the field-strength will decrease inversely as the distance. It is this law which would undoubtedly apply to the qualitative observations reported on page 602 (figure 10), in which the field-strength at 14 to 20 miles by the direct optical path was comparable with that at 4 miles, when the transmission was along the ground and the inverse-square law would apply.

§ 6. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board, and acknowledgment is due to the Department of Scientific and Industrial Research for granting permission for publication. The authors desire to thank Messrs B. J. Byrne and A. C. Haxton for much assistance both in the experimental measurements and in connexion with the various theoretical calculations involved.

REFERENCES.

(1) R. L. Smith-Rose and R. H. Barfield. *Proc. R.S.* **107**, 587–601 (1925).

(2) R. L. Smith-Rose and R. H. Barfield. *J.I.E.E.* **64**, 766–70 (1926).

(3) J. A. Ratcliffe and M. A. F. Barnett. *Proc. Camb. Phil. Soc.* **23**, 288–303 (1926).

(4) R. H. Barfield. *J.I.E.E.* **66**, 204–14 (1928).

(5) (*a*) J. A. Ratcliffe and W. F. B. Shaw. *Nature*, **124**, 617 (1929).
(*b*) J. A. Ratcliffe and W. F B. Shaw. *Nature*, **125**, 926 (1930).

(6) J. A. Ratcliffe and F. W. G. White. *Phil. Mag.* **10**, 667–80 (1930).

(7) R. L. Smith-Rose and J. S. McPetrie. *Experimental Wireless and Wireless Engineer*, **6**, 532–42, 605–19 (1929).

(8) W. Duddell and J. E. Taylor. *J.I.E.E.* **35**, 321–53 (1905).

(9) (*a*) B. Rolf. *Ingeniörs Vetenskaps Akademien*; *Handlingar* No. 96 (1929).
(*b*) B. Rolf. *Proc. Inst. Rad. Eng.* **18**, 391–402 (1930).

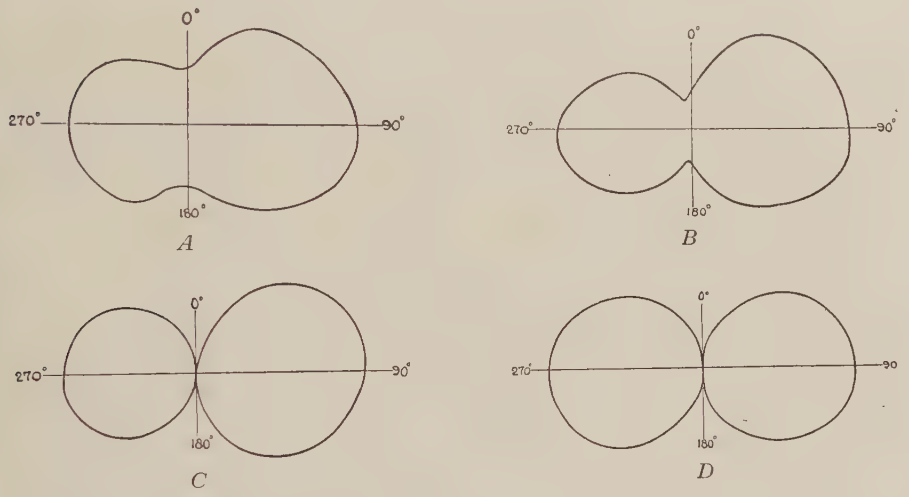
(10) M. J. O. Strutt. *Naturwissenschaft*, **17**, 727–28 (1929).

APPENDIX: AN EXPERIMENTAL DIRECTION-FINDER FOR USE ON ULTRA-SHORT WAVES

Mention has been made in the paper of the fact that observations were made with a direction-finder to ascertain approximately the nature of the field at both short and long distances from the transmitter. It is thought that a brief description of this instrument would be useful as an appendix to the paper.

(i) *Arrangement of d.f. set.* In the field strength measurements recorded above a simple type of closed loop receiver was employed, the circuit of which was shown in figure 2. This whole receiver is placed on a turntable mounted on a tripod and a means is thus provided for the taking of bearings on the transmitter. Since the whole of the receiver, other than the loop, is contained in a screened box, the set is free from the direct pick-up of signals on the valve circuits. Further, it will be seen from figure 2 that the receiving loop is tuned by two condensers in series, the lead between them being connected to the valve filaments and the screening box; also it was found that the capacities between the ends of the loop and the box were of the same order. It might, therefore, be expected that the loop is approximately electrically symmetrical about its midpoint, and would give a satisfactory figure-of-eight cosine diagram for direction-finding purposes. Simple aural tests, however, showed that this was not the case, and that the quality of the signal minima given by the set was much improved by the addition of an electric screen around the loop, in the manner commonly adopted in direction-finders on longer wave-lengths. Accordingly some measurements of the reception characteristics of the set were carried out when the loop was oriented in different directions relative to that of the transmitter.

(ii) *Experiments with screens round loop.* The measurements were made in the manner adopted above. The d.f. set was installed at a distance of 50 metres from the transmitter on the site which had proved most satisfactory for the attenuation measurements described in § 4 (*b*) of the paper. Readings of the audio-frequency output were made for a series of orientations of the set while conditions at the transmitter remained constant on a wave-length of 8 metres. Care was taken that the observer should remain in a fixed position below the set, and a repetition of the measurements over a portion of the 360° showed that the measurements could be made to a reasonable accuracy. A polar reception diagram obtained in this manner for the loop receiver with no screen around the loop is shown in figure 14 (*A*). The two lobes of this diagram are dissimilar and the positions of signal minima are not well defined. When a rectangular framework 15 × 4 in., comprising 50 wires 14 in. long, was placed around the coil, the wires being bonded together but insulated from the metal box, the diagram shown in figure 14 (*B*) was obtained. It is seen that the minima have become a little sharper but the two lobes are still asymmetrical, the strength of signal received on one side of the coil being about 30 per cent. less than on the other side. When the screen was connected to the metal screening box containing the receiver the signal minima became practically zero, as shown in figure 14 (*C*), although the polar diagram was still asymmetrical. By trial of various arrangements of spacing and bonding of the screen wires, it was found that this asymmetry could be compensated for by earthing to the box the wires on one side of the loop while the remainder were left insulated. The polar diagram of the receiver with this arrangement is shown in figure 14 (*D*) from which it will be seen that the two signal zeros are sharp and well defined at positions 180° apart, and that the diagram is approximately symmetrical about the line through the minima. These experiments indicate that the fault with the unscreened loop is that the two sides are slightly out of balance in respect of their capacities to the box, to which the midpoint of the loop is virtually connected, and that this lack of symmetry can be compensated for by a suitable arrangement of the screen wires. It is possible that if the effect of the screen were applied in the reverse sense the asymmetry of the polar diagram of *A* or *B* could be accentuated to produce a unidirectional short-wave receiver, but the experiments have not been continued in this direction.



A. Loop unscreened.
B. Loop surrounded with symmetrical screen, insulated.
C. Loop surrounded with symmetrical screen connected to box.
D. Loop surrounded by screen adjusted to compensate for asymmetry of loop.

Fig. 14. Polar reception diagrams of ultra-short wave d.f. set on wave-length of 8 metres.

(iii) *Performance of d.f. set*. The diagram given in figure 14 (*D*) above shows that when both transmitter and receiver were erected on a satisfactory site the d.f. bearing is very accurate for the distance of 50 metres employed. This was the condition in which the measurements of attenuation illustrated in figures 6 and 7 were measured. When the experiments were repeated on a less satisfactory site it was found that the observed bearings were subjected to erratic variations of the order of ± 15°, which were attributable to the effect of reflected waves from objects local to the transmitter.

The effect of extraneous conditions in the neighbourhood of the transmitter was also demonstrated in some experiments made with the direction-finder when bearings were taken upon the main transmitter at Slough, a half-wave aerial with currents of from 0·1 to 0·5 amp. at the centre being used. The results of these measurements are given in table 2.

As the distance from the transmitter was increased the signal-intensity became rapidly less and at 8 miles the signals were just strong enough for bearings to be taken. At distances of more than 8 miles the signals were inaudible until the receiver was taken to the top of a hill, 500 feet higher than the transmitter, when, as already recorded in § 4 (*c*) of the paper, the signal-intensity at a range of 20 miles was comparable with that at 4 miles along the flat ground, and accurate d.f. bearings were again possible. While some of the errors recorded in the above table were probably due to conditions local to the direction-finder (e.g. at Poyle where the receiver was near telegraph wires) it is evident that there is a tendency for the errors in bearing to be less at a distance of a few miles than close to the transmitter. It was also observed that the signal minima were more clearly defined at a distance, despite the reduction in signal strength which necessarily accompanied the observation. These facts are consistent with the idea that at the transmitter the trees and other objects surrounding it are acting as efficient reflectors, and thus provide an effective source of radiation which is distributed over an appreciable area around the transmitting antenna itself.

Table 2. Summary of results obtained with d.f. set at various distances from transmitter operating on a wave-length of 7·9 metres.

Position of d.f. set	From transmitter		Error in observed d.f. bearing (degrees)
	Distance (miles)	True bearing (degrees)	
R.R.S. (A)	0·12	0	− 17
(B)	0·12	20	− 1
(C)	0·12	300	+ 15
Datchet	0·6	75	− 6
Sunnymeads	1·0	16	− 7
Wraysbury	2·0	342	− 5
Poyle	2·5	307	− 9
Stanwell	4·0	297	− 1
Ashford (A)	7·0	299	0
(B)	7·0	303	− 2
Feltham	8·0	293	− 2

These simple experiments serve to illustrate both the application and limitations of short-wave transmission and direction-finding. Unless the site around the transmitter is clear over a considerable area, reliably accurate bearing observations will not be possible except at distances for which the angle subtended at the receiver by the obstacles surrounding the transmitter is very small. Apart from this, direction-finding on ultra-short wave-lengths would appear to offer possibilities under receiving conditions which have been found to give good results on longer wave-lengths, so long as there is a direct-ray path from transmitter to receiver.

DISCUSSION

Prof. L. S. Palmer. I am, personally, needing to know the nature of the elliptical polarization of the electric vector of the wave near the surface of the earth which is consequent upon the earth's conductivity. A rough calculation from the authors' data, if $\sigma = 10^9$ e.s.u. and $f = 4\cdot 10^7$ for a 7·5-metre wave, leads to an approximate value of 12·5 per cent. for the ratio of the horizontal component of the electric vector to the vertical component. From some measurements at this frequency which I have made recently with a frame aerial I deduce this ratio to be about 14 per cent. over the low wet soil immediately north of Hull. As this figure serves to check other results, I should be very grateful to know if the value of 12·5 per cent. calculated from the authors' data has been directly measured by them. I recollect that Dr Smith-Rose, with Mr Barfield, has done measurements of this kind with a tilting aerial but on longer wave-lengths. Secondly, I would be interested to know if the authors, in designing their radiating frame, gave any special consideration to its dimensions. I think it is quite possible that the strong signals received at Banstead may have been the result of a concentration of the radiation in that direction due to the particular frame-dimensions, which can very appreciably alter the angle at which the radiation leaves the aerial. I think this question would have to be considered as well as the reflected radiation from local trees which the authors suggest. As regards a third and minor point of interest in the question of the transmitter design, I should like to ask whether the screening box referred to in the appendix was of copper. If so, did the authors not have great difficulty in maintaining the oscillations when so much energy was being absorbed in the copper screen? I feel that the authors have obtained data, the real practical value of which will be fully appreciated only when the commercial applications of these short waves are matters of everyday life, and that time may not be very far off.

Mr L. L. K. Honeyball. I should like to ask the authors whether, in the design of their transmitting and receiving aerials for these ultra-short waves, they have explored the possibilities of making aerials of large surface area per unit length of conductor. I notice in the photographs shown that the aerials are of very small dimensions. My own experience in the design of gear for these wave-lengths suggests that there is an all-round gain to be obtained from the use of conductors of this large surface-area in the radiating portion of the oscillatory circuit. Apart from the increase in mechanical rigidity (necessitating the employment of less dielectric material to support the structure) and the obvious decrease in resistance, it is possible by this means to obtain actually a smaller value of inductance with a larger aerial. It seems to me that in the quest for frequencies as high as 5.10^7 or $10^8 \sim$ it is preferable to concentrate on reducing as far as possible the inductance rather than the capacity of the circuit, as any reduction in capacity limits the power and renders the oscillation less stable. Apart from any question as to the optimum dimensions of the aerial in relation to the wave-length, it is clearly better to reduce the inductance by increasing the area of the radiating surface rather than by a general all-round reduction in the size of the aerial. I think it is of importance too that the aerial should be, if possible, of larger dimensions than the rest of the apparatus associated with it, even if the latter is screened or the former is fed by a high-frequency line.

AUTHORS' reply. In reply to the first of Professor Palmer's questions: no measurements have yet been made by us of the relative values of the vertical and horizontal components of the electric vector near the surface of the earth on the short wavelengths in question. While the tilting-aerial method as employed on longer wavelengths might be used for such measurements, it is doubtful if the method would be accurate enough to distinguish between the values of 12·5 per cent. and 14 per cent. mentioned by Prof. Palmer. It must be remembered that for a complete specification of the electric field at the earth's surface the value of the dielectric constant is required in addition to that of the conductivity. Our own experiments are being continued on these and higher frequencies with a view to evaluating these constants with greater accuracy.

Although we are aware of and appreciate very much the work carried out by Prof. Palmer and Mr Honeyball on the use of low-inductance loops for short-wave transmitters, we have not yet had an opportunity of applying them to our own investigations. In the case of the reception of signals at Banstead, mentioned in the paper, the transmitting antenna was a half-wave vertical dipole fed by a transmission line from a loop inside a screened hut. The question of the non-uniformity of radiation around a loop did not, therefore, arise, and the angle of elevation of the radiation above the ground was less than one degree. For the short-distance measurements we particularly desired a radiating loop of small area so as to simulate a point source. The use of specially designed loops of large surface area and low inductance, mentioned by Mr Honeyball, is worthy of consideration, and it is probable that such loops may have important applications to directional receivers as well as to transmitters.

We have usually employed tinned iron sheet for our screening boxes and have not experienced any great difficulty, due to absorption of energy in the screens, in maintaining oscillations. A more serious difficulty is that of keeping the dimensions of the screens and boxes small compared with the wave-lengths in use.

PRESENTATION OF THE DUDDELL MEDAL *to* SIR JOHN AMBROSE FLEMING, M.A., D.SC., F.R.S.

AT the Annual General Meeting of the Physical Society, held at the Imperial College of Science, South Kensington, on Friday, March 20, the President of the Society, SIR ARTHUR EDDINGTON, F.R.S., presented the Duddell Medal of the Society to SIR JOHN AMBROSE FLEMING.

Sir Arthur Eddington, in making the presentation, spoke as follows: A careful review of the contributions to science and technology which have led to this award has been drawn up by those best qualified to judge, and I shall base what I have to say on their memorandum. We cannot sum up in a sentence researches extending over an active career of 50 years, but in general we may say that the work of Sir Ambrose Fleming has lain in the applications of electrical science, and perhaps particularly in the invention of instruments for exact measurement.

Educated at University College, London, the Royal College of Chemistry, and St John's College, Cambridge, he held for some time a lectureship at Cambridge in applied mechanics. From 1877 to 1879 he was working in the Cavendish Laboratory on a comparison of the British Association resistance coils and the standard British Association units—a work undertaken at Clerk Maxwell's suggestion. For this purpose he designed in 1879 a special form of resistance balance, which was in use there for many years for comparing standard coils. He also designed a special form of standard coil capable of taking up quickly the temperature of the water in which it was placed.

In 1882, when practical incandescent electric lighting began, his attention was turned to the need for quick and accurate workshop methods of electrical measurement. He made in 1883 the first direct-reading potentiometer, set to read current and potential directly in amperes and volts. He described this method in a journal which is now defunct. The method was almost immediately copied in various forms by all electrical instrument makers.

In connexion with incandescent lamp manufacture by the Edison and Swan Electric Lighting Company, Sir Ambrose Fleming designed in 1895 a form of large bulb incandescent lamp as a standard of light more constant and easy to use than the flame. This has been much used since. When alternating-current working began in 1883, and the alternating-current transformer began to be used, the necessity arose for careful determination of efficiencies. He designed a form of wattmeter for this purpose, with which he made extensive researches on transformer-efficiencies; these were reported to the Institution of Electrical Engineers in 1892. In this paper he first suggested the use of the term "power factor' which at once came into everyday use.

When practical wireless telegraphy first began under Marconi in 1898 no appliances were obtainable for measuring wave-lengths and frequencies. In 1904

Sir Ambrose Fleming invented a simple instrument for this purpose, which was capable also of measuring small capacities and inductances. In conjunction with Prof. Clinton he also devised a rotating commutator for measuring the capacities used in wireless. In 1904 he invented his now famous 2-electrode thermionic valve, which provided at once a simple detector of wireless waves, far more easy to manage than the coherer then in use. It prepared the way for a subsequent improvement, the 3-electrode valve, which is now the most important weapon of the radio engineer, and without which wireless as we now have it would not exist.

In 1905 he described to the Physical Society an instrument called the campograph, which enables curves such as the hysteresis curve of iron to be delineated optically without the tedious procedure involved in other methods.

Between 1892 and 1895 he co-operated with Sir James Dewar in a remarkable series of researches on the electric and magnetic properties of matter at low temperatures, including the great increase of electric conductivity which accrues. He devised special forms of resistance-coil and instruments for the measurement of inductance, capacity and thermo-electromotive force. I may remind you of the immense advance in modern theoretical physics to which the study of low temperatures has led.

He was Professor of Electrical Engineering at University College, London, for 42 years, and he established there the first laboratory for high-frequency and radio measurements. Besides his papers in scientific journals, he has published many books and treatises on applied electricity. It requires no great imagination to appreciate the importance of the numerous instruments of measurement designed by Sir Ambrose Fleming for use in the electrical industry generally and for scientific research, but I think there is one invention which comes uppermost in all our minds. I understand that the psychologists or psycho-analysts for their mysterious purposes sometimes fire at their victim a word or name which he has to respond to instantly by naming the first associated idea which comes into his head. If in this way I pronounce the word "Fleming," the instantaneous response is "valve," or we may vary the procedure and put it the other way round, and say when the word "valve" is mentioned, "Oh, Fleming, of course." The discovery of the 2-electrode valve in 1904 has paved the way for the great development of wireless to-day and so has led to one of the greatest influences of science on our civilization. This gift of science we can contemplate without those mixed feelings with which, for example, I should regard the telephone or the motor car, which sometimes occasion our gratitude and sometimes occasion our profanity. I do not suppose that Sir Ambrose foresaw all the strange results that would ultimately come from these experiments carried out in University College 25 years ago. As we sit here unheard voices are all around us; from all parts of the earth they speak. As in the magic Isle of Caliban,

> . . . the isle is full of noises,
> Sounds and sweet airs that give delight and hurt not,
> Sometimes a thousand twangling instruments
> Will hum about mine ears: and sometimes voices . . . .

I think it might be safest to end the quotation there, because Shakespeare is sometimes a little too apt. But if those in this audience who from time to time give talks before the microphone will shut their ears, I will complete the quotation:

> . . . that, if I then had waked after long sleep,
> Will make me sleep again.

It is a proud distinction to have been one of those responsible for an essential part of this device, to have overcome one of the major obstacles to the fruition of those ideas which started with Maxwell and Hertz. There are names which we honour in connexion with the pure theory. We honour in a different way, though no less sincerely, those who by breadth of vision developed a scientific toy into something of world-wide service. Intermediately we honour those who by their skill in turning the results of scientific discovery into practical invention bridged the gulf, and among those the name of our medallist stands out conspicuously.

Now I turn to a feature of the award to which I have up to now deliberately suppressed all reference. I have, so to speak, placed our medallist on the dissecting table, and tried to show you from his writings and inventions what manner of man he is. But Sir Ambrose Fleming is not altogether a stranger to the Physical Society. He is one of ourselves. In fact, if I may so put it, he is one of ourselves more than any of us.

To go back to a period when the age of the present speaker belonged to the domain of negative numbers, Fleming was one of the original members of this society, and in March, 1874, he read the first paper at the first meeting of the society, his subject being, "The new contact theory of the galvanic cell." That was a good start, and he kept it up. During the ensuing 40 years he contributed regularly to our *Proceedings*—35 papers in all, amounting, I suppose, to about one-third of the total of his published papers. Once a year the occasion of the award of the Duddell Medal gives the society the pleasure of recognizing and honouring distinguished merit. It is a double pleasure when the honour falls to one of our intimate colleagues in the society. It is a triple pleasure, a manifold pleasure, when it falls, as it does on this occasion, to a founder of the society, whose papers started our scientific proceedings, and who has been loyal to the society during the 57 years of its existence.

Turning to Sir Ambrose Fleming, Sir Arthur Eddington said: Sir Ambrose, your life-work survives and bears fruit in the great electrical industries of the world. Your monument is in the circumambient ether. But you will not despise this mark of recognition and appreciation from the society of which you have so long been a member. In handing you the Duddell Medal I would express to you on behalf of the Physical Society its esteem for your achievements as a man of science, its regard and affection for you as a colleague, and its good wishes for your continued health and enjoyment.

Sir Ambrose Fleming, after expressing his thanks, added: It has been my good fortune for now 50 or more years, since this society was founded, to have been closely connected with the introduction into Great Britain of four scientific inventions which have subsequently founded great industries: the telephone, the incandescent electric lamp, the alternating-current transformer for high-tension working, and wireless telegraphy. When I went up to Cambridge in 1877, with the chief object of working under Maxwell in the then recently completed Cavendish Laboratory, the telephone had just been invented by Graham Bell, who, by the way, was not an American, but an Englishman, or rather a Scotsman, although naturalized in America. Edison had added to that invention by inventing the carbon button transmitter. The Bell telephone was a good receiver, but a poor transmitter; Edison, therefore, availed himself of the discovery of the alteration of the resistance by means of a button of carbon made of lamp black, but he had no receiver, and had to invent a curious receiver, a chalk cylinder, moistened with various chemicals, which one had to keep on turning whilst one listened to it.

In 1878 David Hughes invented the microphone, and described it in a paper to the Royal Society. He did not patent it but placed it at the disposal of the public generally, and so the Bell Company availed themselves of this. Edison considered that that was an infringement of his rights, so the way was prepared for a nice quarrel, and the question was whether the microphone acted on the principle of the Edison arrangement. As a matter of fact, what the microphone did was to make small jerks and vibrations audible through a Bell telephone. An experiment which was very popular at that time was to put a domestic fly into an empty matchbox and to put on the outside a microphone connected with a battery, when one was supposed to hear the fly marching about with a tramp like that of an elephant. As a matter of fact, it was sometimes found when the matchbox was opened that the fly had been dead for some time. The noises heard with the microphone were due to agitations of that instrument by little movements in the room and so on. Some people even wondered whether it might be used to detect an incipient earthquake. I was brought into the arguments as to whether the Edison button was different in its mode of action from the microphone. As I say, the stage was set for a great quarrel, but the two telephone companies had soon to turn their faces towards a common enemy, namely, the Post Office, which claimed that the instrument could not be used without the payment of royalties to itself. That necessitated a very important action, and nearly all the eminent people of that day were engaged as witnesses either for or against the Crown. It was a question of the interpretation of certain words in an Act of Parliament.

At about that time Swan and Edison had patented the invention of the incandescent lamp. Edison sent to England two of the earliest samples of the carbon filament lamp, and his agent instructed me to show the action of these lamps in the offices of the Edison Telephone Company. The only thing that is worth remembering in that connexion is to show how one's memory sometimes fails one. Years after that, when we were engaged in fighting patent actions, it became necessary to know when the first lamps came over from Edison to London, and I was asked whether I knew anything about it. I had completely forgotten this early occurrence, and I said, "No." Then the secretary of the company which brought forward the Edison lamps said in reply to a question that the only man who knew anything about this first introduction was Fleming, and with that it all came back to me in a flash that in 1879 these specimens of the earliest lamps had been sent over to me.

Electric lighting began on a small scale. The first station established by the Edison people was in the basement of a house at No. 57, Holborn Viaduct. In those days we thought it a great thing if a machine ran through the night without a breakdown. The late Dr John Hopkinson, who was appointed scientific adviser with me, directed his attention to improving the design of the Edison dynamo. I devoted my attention to the lamp, and I will show you one slide which is interesting because it indicates the starting point for a number of other observations. My attention was directed to the fact that these lamps in some cases were blackened uniformly, while in other cases there was a curious white line which was in the plane of the filament, and when the filament came to be examined it was generally found to have been broken on the opposite side. In other words, there had been a projection of carbon in straight lines. In the majority of cases there was a volatilization of carbon from the filament generally. The next thing I found out was that on putting a metal plate into the bulb of a lamp and sealing it into the bulb, an expulsion of negative electricity took place from the filament. In those days we knew nothing about the electron; it was 10 or 12 years before the experimental discovery of the electron by Sir J. J. Thomson. I was astonished to find what an enormous quantity of electricity came off the filament. If I connected up with wire to the positive terminal of a large condenser the charge disappeared. The question was, where did that electricity come from? The founder of this society made the discovery that an iron ball heated red hot would hold a charge of negative electricity, but not of positive. I thought the phenomenon might be connected with the carbon, that the carbon particles thrown off carried a negative charge. I found that the greater part of the negative charge came off from the negative end of the filament. Here I show you one lamp which was covered with a deposit. Edison fastened the carbon to the platinum wires, and you will see that in one place there is a line in which there is no deposit, and that line is in the plane of the filament.

The next experiment I made was to construct a lamp with two filaments in it, and I found out that if one of those filaments—the positive—was rendered incandescent and not the other, then many thousands of volts were necessary to send the smallest current; but if the negative filament was rendered incandescent even one volt would send a current. It occurred to me that a bulb of this kind might act as a valve; if one of the carbon filaments was made incandescent, electricity could be sent in one direction and not the other.

All these observations were made between 1895 and 1896, and in a long paper which I presented to this society in 1896 I described these experiments. I also gave a discourse on the subject at the Royal Institution. But there the matter ended until wireless telegraphy came into the field. In 1897 Marconi came over with a new plan for conducting wireless by means of Hertzian waves. He had put together a number of old elements, which he had improved, and out of them he had made a practical system of telegraphy. His first achievement was to get across the English Channel in 1899. He then covered the longer distance between the Isle of Wight and the Lizard. But he was anxious to conquer the Atlantic, and that, he knew, would require greater power. Therefore, as I had been connected with the old London

Electric Supply Corporation, he asked me to design for him the arrangements for making powerful oscillations. I show a photograph of the first plant I arranged for him in the early stages of the Poldhu experiment.

On December 12, 1901, Marconi got his first signals across the Atlantic. Before that time we had often discussed whether it was possible to do that. We knew nothing in those days about the Heaviside layer, and my own view was that the chief objection would be the curvature of the earth. I repeatedly impressed on Marconi that he must lengthen the wave as much as possible. About that time I designed the cymometer by means of which we were able to measure the length of the waves actually used.

The question of detectors next came up. The early work was done with the coherer and telephone, but the coherer was troublesome to use and was very easily upset by atmospherics and by oscillations near it. I wanted to get hold of a receiver of some kind which would not be affected by atmospheric conditions or by powerful discharges in its neighbourhood. It was obvious that one would have to rectify the high frequency oscillations, and after trying a great many experiments with chemical rectifiers which did not work, my own experiments with these lamps came back into my mind, and I constructed a lamp in which the filament was surrounded by a cylinder. The space between cylinder and filament was unilaterally conductive. Under the influence of a battery it became useful for rectifying oscillations. I show you one of the first of these which was made for the Marconi Company. My attention was taken up at that time with other matters, and unfortunately I did not go on to put in the grid as I ought to have done. In America De Forest put in the first grid. Curiously enough, I had put a grid into a bulb, and you will see here a photograph of it, also a plate in another bulb, but what De Forest did was to put the two together into one bulb. Here is one of his receivers, and that at once made an amplifier. Soon after I constructed a 3-electrode valve with a spiral as the grid, which was the forerunner of the modern valves. It did not precede what De Forest did. That was the 3-electrode amplifying valve from which everything else has evolved.

My chief point is that the whole of these practical discoveries resulted from this single observation of the white line on the lamp which was otherwise covered with carbon.

I apologize for keeping you so long with these memories of early work, and I beg you to accept once more my sincere thanks for the great distinction you have conferred upon me by the gift of this Duddell Medal.

Prof. H. E. Armstrong, who was invited by the President to add a few words, said: I have known my friend Fleming since he was a student in this college with Guthrie. He set an example from the very beginning, and I think all of us who have known him have loved him sincerely. Among scientific men he has always ranked high on account of his extraordinary devotion to his work and his honesty in putting it forward.

Sir Ambrose Fleming and I can overlook practically everything that has taken place in the development of electricity. As he has told you, the dynamo at the beginning was a very miserable machine, until Hopkinson took it in hand, and it had not been turned round and made into the efficient motor machine that we know to-day.

Not only have we witnessed in the period of which Sir Ambrose Fleming has been speaking the whole development of applied electricity, but we have seen scientific development in many other fields. For example, we have witnessed the age of the ironclad. The first ironclad, the *Warrior*, was built in 1860; I saw her in 1865 at Gibraltar, alongside the *Marlborough*, which was the last of the wooden three-deckers. I saw the *Great Eastern* when she declined to be launched on the stocks at Greenwich, and, as you know, she laid the first efficient cable. Then there has been the development of the internal combustion engine. I have an acute recollection of our troubles at the City and Guilds of London Technical College at Finsbury in the early days; how, for example, the piston had a habit of falling down backwards. I recollect, too, a most terrible quarrel between Ayrton and someone at Birmingham—Smith or Brown, I think, was the name—over this machine. It was a truly awful machine.

One may say that one has seen a whole vast development of scientific knowledge and its application to machinery in general, all in the space of about 60 years, and I think that is a matter that we ought to reflect upon a little more than we do. We do not sufficiently realize the astounding rate at which man has gone forward since he has learned to use the experimental method—the method in which your medallist has shown himself to be such a master. The world is in no way alive to the fact that we have discovered a new method, because it is practised only by the few, and nearly all of them engineers. We have been so much concerned with improvements in machinery, that we have forgotten the most important machine of all, that is to say, ourselves. We have not touched the politician, we have not touched government in any shape or form. I should like to see carried out a suggestion which was made by a bishop a few years ago, and put these interfering scientific inventors to sleep for a time, while we have leisure to think of other things. It seems to me that unless we can do that we shall be overcome by our own creations. Although we have to congratulate ourselves on this astounding development of the experimental method as applied particularly in physics, we have to bear in mind that there is this very much more important work awaiting our direction.

OBITUARY NOTICES

PROFESSOR H. L. CALLENDAR, C.B.E., M.A., LL.D., F.R.S.

HUGH LONGBOURNE CALLENDAR, eldest son of the Rev. Hugh Callendar of Magdalene College, Cambridge, was born at Hatherop, Gloucestershire, on April 18, 1863, and died at Ealing on January 21, 1930. He entered Trinity College, Cambridge, from Marlborough in 1882 and was placed in the First Class in the Classical Tripos, in 1884 and in the First Class in the Mathematical Tripos in 1885. He was appointed Professor of Physics at Montreal in 1893, at University College, London, in 1898 and at the Imperial College of Science in 1902.

Elected a Fellow of Trinity in 1886, he became a Fellow of the Royal Society in 1894 and Rumford Medallist in 1906. He was Treasurer of the Physical Society from 1900 to 1909, President during the period 1910–12 and first Duddell Medallist in 1923.

There is good reason to believe that Callendar regarded platinum thermometry and his investigation of the thermal properties of water and steam as his greatest achievements. It therefore seems appropriate that a brief tribute to his memory should confine itself to these aspects of his work.

Callendar's development of the platinum thermometer, which made it a standard instrument, is familiar to every physicist. Not the least of the virtues of such thermometers is the ease and certainty with which, by the use of two of them, the difference between one temperature and another can be determined from a single reading.

Callendar quickly saw the advantages of continuous flow methods in calorimetry and developed these in practice with extraordinary skill and ingenuity. In such methods there are no discontinuities due to the stopping or starting of the flow. The water equivalent of the apparatus is not required. The heat-loss can be reduced to a minimum and its magnitude can usually be obtained, as accurately as desired, by varying the speed and other conditions of flow. The Joule-Thomson porous-plug or throttling experiment is an early example of a continuous flow device to which, incidentally, Callendar applied differential platinum thermometry with conspicuous success.

Callendar applied a similar principle when he invented the continuous flow method of measuring the specific heat of water, used by Barnes and himself. At a later date, when the accuracy of the results obtained in these experiments was questioned, he showed his unfailing ingenuity by devising and using what was, in effect, an adaptation of continuous flow to the time-honoured "method of mixtures" familiar to every student of physics.

Another application of the same principle led to the determination of the specific heat of steam. This determination, in conjunction with that of the cooling effect in throttling experiments, enabled him to measure the variation with pressure of the total heat of steam. At a still later date he devised a general method of measuring the total heat at any pressure and temperature. Briefly, this method consisted in throttling to any desired pressure at constant total heat and then measuring, in a continuous flow calorimeter, the heat removed when the steam was reduced to water at measured temperature, of which the total heat was known. The same method was used to find the total heat of water, at any temperature and pressure, with reference to that at some temperature and pressure taken as standard. It was also applicable to wet steam.

With high courage Callendar set himself the task of measuring total heats in this way up to and beyond the critical region. The results are of the greatest interest. Before this work was done it had been commonly supposed that, at the critical point, the differences between saturated steam and water disappear. The specific volumes, it was thought, were then identical and the latent heat of vaporization zero. As is well known, the simplest method of determining the critical temperature of a liquid is to heat an appropriate amount of it in a sealed glass tube and to note the temperature at which the meniscus separating liquid from vapour disappears. This method presents no difficulties with substances like CO_2 and SO_2; but until fused-quartz tubes became available it was impracticable to apply it to water owing to the disintegrating effect of the latter upon ordinary glass.

In agreement with other observers Callendar, using quartz-glass tubes, found the critical temperature of water to be 374° C. Using different quantities of water in separate tubes of similar volume, he also obtained values for the densities of the liquid and the saturated vapour at temperatures below the critical point by observing the temperatures at which the tubes became filled with the liquid or the vapour as the case might be. In order to get consistent results in such experiments, it was necessary to use very pure water free from air.

Similar experiments can be performed very easily with liquid SO_2 instead of water. In this case ordinary glass suffices and the critical temperature and pressure are so much lower than those of water that there is neither difficulty nor danger in observing what happens in a series of tubes like those used by Callendar. Indeed, some of my old students of thirty years ago will remember this as a laboratory exercise devised for their instruction. Anyone who has performed such experiments and compared the phenomena with those exhibited by liquids which do not mix at ordinary temperatures, but become miscible in all proportions at higher temperatures, will agree with the view that the temperature at which the meniscus vanishes, in the case of a single substance in the tube, is not necessarily that at which the liquid and vapour phases become identical. It required the determination and the experimental skill of Callendar, however, to produce quantitative evidence. He found, for example, that the latent heat of vaporization of water at the critical temperature is not zero but 72·4 cal./gm. Not until a temperature of 380·5° C. is reached does the latent heat vanish. In obtaining these results, based upon measurements of total heat, special methods had to be devised in the case of water to avoid contamination by air, traces of which were enough to make accurate determinations impossible.

Any attempt to indicate the character of Callendar's work on steam must contain some reference to the analytical skill which he displayed on the theoretical side. Almost every equation he used to correlate his results had a reasonable, if not an entirely "rational," basis. His equations, unlike those of his predecessors, were all consistent with the laws of thermodynamics.

One of the earliest applications which he made of platinum thermometry was to the study, at Montreal in conjunction with Nicolson, of the law of pressure temperature variation in the adiabatic expansion and contraction of dry steam. This led him to the formulation of his well-known characteristic equation for an imperfect gas, which, in its earliest form,

v, p, θ, n

$$v - b = R\theta/p - a/R\theta^n,$$

was a modification of the Rankine-Thomson equation. Following previous workers, he replaced v by $(v - b)$. The novelty lay in the substitution of θ^n for θ^2 in the last term.

Assuming, as the simplest hypothesis suggested by the kinetic theory, that the variable part of the internal energy u of a gas is proportional to $p\,(v - b)$ and applying the second law of thermodynamics, Callendar deduced from this equation the expression

$$u = np\,(v - b) + \text{const.}$$

and expressions for n in terms of definable quantities, of which the simplest are

$$n = (c_v)_0/R, \quad \text{and} \quad (n + 1) = (c_p)_0/R,$$

$(c_v)_0$, $(c_p)_0$ — $(c_v)_0$ and $(c_p)_0$ being the values to which the specific heats at constant volume and constant pressure, respectively, approach when the pressure is reduced without limit.

It also followed that the pressure temperature variations for adiabatic changes should be given by the equation

$$p/\theta^{n+1} = \text{const.}$$

This was in accord with the experimental results for dry steam and the experimental value for n did not differ greatly from that calculable from the kinetic theory by a "reasonable" method.

H, ϕ — Correspondingly simple expressions for the total heat H and the entropy ϕ were:

$$H = (n + 1)\,p\,(v - b) + bp + \text{const.} \qquad \text{......(1),}$$

$$\phi = (n + 1)\,R \log \theta - R \log p - ncp/\theta + \text{const.,}$$

c — in which c represents the value of $a/R\theta^n$.

It was characteristic of the man that he should try to find a simple physical interpretation of c.

Writing his equation in the form

$$v - b = R\theta/p - c,$$

he pointed out that $R\theta/p$ represents the volume which the vapour would occupy if the effective volume were correctly represented by $(v - b)$ and if the vapour behaved like an ideal gas, consisting of molecules of the simplest possible type, R being the appropriate gas constant. The presence of the term c shows that the actual volume is less than the ideal volume. He suggested that the discrepancy is due to the fact that the vapour does not consist wholly of simple molecules but contains also a certain proportion of molecular aggregates. Increase in the number of such "molecules" of greater mass would cause $R\theta/p$ to become increasingly greater than the ideal volume. In this interpretation, inter-molecular forces do not appear explicitly. They are replaced by molecular complexes of which, however, they may be the cause.

Another striking example of Callendar's ingenuity is his equation for the total heat of water, which he used with great success in his correlation of the facts. To obtain it he developed a particular form of an argument previously used by Poynting, and assumed that water in equilibrium with its saturated vapour contains the same number of vapour molecules per unit volume as the vapour itself. He then supposed that the formation of such vapour molecules, within the liquid, consumed the same amount of heat as would be required to produce the corresponding volume of steam. Hence his equation

$$h = st + wL/(v - w) \qquad \text{......(2)},$$ h, t

expressing the value of the total heat of water at $t°$ C. reckoned from that at the freezing point as zero. In this, w and v are the specific volumes of the water and the w, v
saturated vapour respectively, and L is the latent heat of vaporization, at the L
temperature t. The constant s was fixed by taking h to be 100 calories at 100° C. t

The equation leads to an expression for the entropy of saturated steam which, with the expressions for H and ϕ already mentioned, gives an equation connecting the saturation pressure of steam with the temperature. This well-known equation contains nothing, in addition to b and c, that is not directly measurable, and is in close accord with experiment up to 200° C. Beyond this, the experimental results began to deviate appreciably from those calculated and it became necessary to regard c as a function involving the pressure as well as the temperature.

In order to maintain thermodynamic consistency between the equation of state and the expression for the internal energy, it is necessary that the relation between c and p should satisfy certain conditions. From the many possible forms which the relation might take, Callendar selected the simplest for his purpose. It is contained in the equation

$$(v - b) = R\theta/p - c/(1 - Z^2) \qquad \text{......(3)},$$

in which $c = a/R\theta^n$ as before and $Z = kcp/\theta$, where k is an additional constant. Z, k

He found that the experimental curve for the density of the saturated vapour could be represented by this equation right up to the critical temperature without alteration of the value of c, provided that the value of the constant k were chosen to fit the density at that temperature. Further, the temperature pressure curve for saturated vapour, the easiest of all the curves to determine experimentally, gave values which were in close agreement not only with those which could be deduced from his theoretical equation, but also with those obtained by other observers, by other methods, up to 374° C. The theoretical equation continued to give values of p agreeing with those observed by himself, until the temperature at which saturated steam and water become indistinguishable was attained.

Finally, the equation

$$(H - st)/(h - st) = v/w,$$

in which $H = h + L$, following at once from equation (2), gave a relation connecting total heats and specific volumes, which was used with success to test the accuracy of the measurements made in the critical region.

Callendar's last words on the practical aspects of this great work, which he pursued untiringly, will be found in his Hawksley Lecture delivered to the Institution of Mechanical Engineers shortly before his death. Referring to his three fundamental equations—(1), (2) and (3) above—he said: "They constitute the only rational and consistent standard which has yet been proposed for steam, and would suffice for all practical requirements if they were generally adopted."

Beyond doubt it was conviction and not dogmatism which impelled him to use these words, just as it was resignation and not impatience which led him to add: "But it has taken thirty years to reach international agreement with regard to the temperature scale, which is a much less exacting problem, and we may have to wait a long time before other nations are prepared to accept such a simple and unpretentious scheme."

Great designs require great consideration.

S. W. J. S.

PROFESSOR A. A. MICHELSON, Sc.D., LL.D., Ph.D.

When Michelson delivered the sixth Guthrie Lecture before the Physical Society in March 1921, more than one man of middle age who heard him felt it strange to see a man apparently no older than themselves who yet had seemed almost an historical personage in their own college days. It was indeed difficult to believe that this alert, vigorous, black-haired man had with Edward W. Morley published the famous paper "On the Relative Motion of the Earth and the Luminiferous Æther"(1) in the year of Queen Victoria's Jubilee, 1887. Yet he had been working at his first attempt as early as 1881(1).

Of the milestones in Michelson's life journey Sir Oliver Lodge(2) has left little to be said. I repeat the passage here, with some omissions and a few additions from various sources(3).

Albert Abraham Michelson was born in Strelno, Poland, on December 19th, 1852. In 1854 his parents brought him with them when they migrated to the United States, making the long journey across the western prairies to Virginia City, Nevada, in the days before the railroads. By the time that he was ready for high school his parents had moved to San Francisco, and on leaving high school in that city, at the age of seventeen, he went alone to Washington and persuaded President Grant to give him a presidential appointment to the Naval Academy at Annapolis, from which he graduated in 1873. After his graduation he served two years as a midshipman and then became instructor in physics and chemistry at Annapolis under Admiral Sampson, continuing this work until 1879. At that time he was not particularly interested in science but, determined to do a good job, he soon began experimenting and devising his own apparatus. Because there was no appropriation for material, Ensign Michelson spent ten dollars of his own money to construct an apparatus to measure the speed of light in a class-room demonstration. To his great surprise, he was able to make the measurement with greater accuracy than had ever before been achieved.

With his interest in science thus aroused, after a year in the Nautical Almanac Office at Washington Michelson went abroad for further study at the universities of Berlin and Heidelberg, and at the Collège de France and the École Polytechnique in Paris. Upon his return to the United States in 1883 he became professor of physics in the Case School of Applied Science, Cleveland, Ohio.

It was while he was at Cleveland that Professor Michelson collaborated with Professor Morley in their joint experiment, which was first carried out in 1883, and it was for the purpose of that experiment that Michelson invented his particular form of interferometer, with the to-and-fro beams at right angles. Later, he applied it in Paris to the determination of the metre in wave-lengths of light. The way this should be done had been first described in a paper by Morley and himself in 1887(4), though an actual attempt to make the wave-length of sodium light a standard of length was made by Peirce in 1879(5).

After six years at Cleveland, he was called in 1889 to Clark University, where he remained as professor until 1892. Then President Rainey Harper, on the look-out for promising men, brought him to the newly founded University of Chicago as Professor of Physics and Head of the Department. In June 1925 he was appointed to the first of the Distinguished Service Professorships made possible by the new development programme of the university.

During the world war Professor Michelson re-entered the naval service with the rank of lieutenant-commander, giving his whole time to seeking new devices for naval use, especially a range-finder which became part of the U.S. Navy equipment.

In 1924 he undertook a very accurate determination of the velocity of light, using Mount Wilson and San Antonio, 22 miles apart, as the stations. He remained in active work at the University of Chicago, engaging in both research and teaching, until he became seriously ill in the autumn of 1929, and underwent two operations. Upon his recovery, he asked to be relieved of active duties and took the status of Professor-emeritus on July 1, 1930. That summer he went to Pasadena, California, to repeat for the last time his famous experiment on the velocity of light. Finding the climate agreeable, he decided to establish a permanent residence in California. The university, however, continued to support his researches, and provided him with a technical assistant who built and installed equipment for the experiment.

Sir Oliver Lodge's article gives a lucid account of Michelson's achievements, but for members of the Physical Society a short reminder of the most important of them will suffice. In presenting the Duddell Medal for 1929 to Michelson, the President said:

"The interferometers invented by Professor Michelson, of which the first was used for carrying out in 1887 the famous Michelson and Morley experiment, have been applied by him, always with complete adequacy of design, to other important and difficult problems, most of them of audacious novelty. These problems included the measurement in 1892 and 1893 of the metre in wave-lengths of light(6): the measurement of the diameters of stars: the re-measurement of the earth tides: and the testing of the effect of the earth's rotation on the velocity of light(7). These measurements have had great consequences, of which the following examples may be mentioned:

"The difficulties of reconciling the result of the Michelson-Morley experiment with the then prevailing physical conception of the nature of the universe were the direct cause of the enquiry of Albert Einstein(8), which resulted in the theory of relativity. The measurement of the metre in wave-lengths of light(9) resulted in establishing a standard of length free from the uncertainty concerning possible variation which attaches to all material standards. The interferometer for the measurement of the diameter of stars, suggested by Michelson in 1890(10) and first applied by him to Betelgeuse(11), has not only confirmed the correctness of the previously almost incredible dimensions yielded by indirect means of calculation, but has detected fresh stellar phenomena in the variable diameter of Mira Ceti, and effected the separation of double stars too close for resolution by the telescope.

"The invention by Professor Michelson of the échelon diffraction grating(12) provided physicists with a potent tool for the investigation of the fine structure of spectral lines, knowledge concerning which has become of such great importance in modern physics. Professor Michelson has also designed a ruling-engine with which very large gratings have been ruled.

"As a final example of Professor Michelson's work on scientific instruments for the advancement of knowledge, mention may be made of the completion by him in 1926, with apparatus designed by himself, of a re-determination of the velocity of light(13). The elaborate precautions taken to secure freedom from error included means whereby the distance of 82 miles* traversed by the light was measured to a higher degree of accuracy than had ever been reached in triangulation."

An account by Michelson himself of his work in the years immediately preceding 1921 will be found in the sixth Guthrie Lecture(14).

In 1921, at the suggestion of Dr L. Silberstein, Michelson arranged an "ether-drift" experiment, in which the effect looked for was that which would be due to the rotation of the earth. The result, published in 1925, was in Michelson's opinion a positive one(15), confirming the existence of a stagnant ether. The writer of this notice has not seen any informed comment on this interesting result.

Professor Michelson before resigning his position at the University of Chicago had already worked at Mount Wilson Observatory, and a brief account of repetitions of the famous Michelson-Morley experiment, with a diagram of the apparatus, was contributed to *Nature* of January 19, 1929, by him and his collaborators. The results then obtained showed no displacement of the interferometer fringes so great as one-fifteenth of that to be expected on the supposition of an effect due to a motion of the solar system of three hundred kilometres per second through the ether.

His last work was concerned with a further determination of the velocity of light. This was described by the President of the Société française de Physique, Professor M. A. Cotton, in announcing Michelson's death to that Society, in the following words:

"Parmi les constantes physiques importantes, il en est une à laquelle la théorie de la relativité, comme le faisait déjà la théorie électromagnétique, assigne une place à part: c'est la valeur de la vitesse de la lumière. Michelson a consacré à plusieurs reprises à la mesure précise de cette vitesse toute son ingéniosité et son extrême habileté expérimentale. C'est cette mesure qu'il s'est appliqué encore à perfectionner durant les dernières années de sa vie, pendant lesquelles il a conservé toute son activité. Michelson avait décidé hardiment cette fois de supprimer la cause des petites erreurs qui peuvent persister toujours dans les mesures les plus soignées de la vitesse de la lumière, lorsqu'on les fait à la surface de la terre: celles qui proviennent du défaut d'homogénéité optique de la colonne gazeuse traversée par le faisceau lumineux, de ces variations de l'indice de réfraction de l'air qui font déjà le tourment des astronomes. Il avait donc décidé de faire le mesure dans le vide. Aussitôt remis d'une grave maladie qu'il avait éprouvée au début de l'hiver de 1929 il était retourné en Californie pour mettre en œuvre les puissants moyens qu'il avait su réunir. Mettant à profit une subvention de 750,000 francs provenant à la fois de la

---

* Subsequently reduced to 22 miles in view of effects of smoke.

Fondation Rockefeller et de la Carnegie Corporation, utilisant les ressources de l'Observatoire du Mont Wilson, il installa sur un terrain approprié, dans la propriété de James Irvine, à 6 milles de Santa Ana, un tube d'acier de 1,610 mètres de long, de 91 centimètres de largeur, formé de morceaux de 20 mètres, avec des joints étanches: c'est dans l'intérieur que le faisceau lumineux poursuit sa route, parcourant plusieurs fois, grâce à des réflexions auxiliaires, la longueur de la base, avant de revenir sur le miroir tournant. Le dernier Rapport de l'Observatoire du Mont Wilson indique qu'on avait réussi à faire dans le tube un vide déjà satisfaisant et que les mesures allaient être commencées. Elles étaient terminées, assure-t-on, et Michelson faisait les calculs qui s'y rapportaient, lorsque la mort est venue le surprendre, en plein travail, à soixante-dix-huit ans."

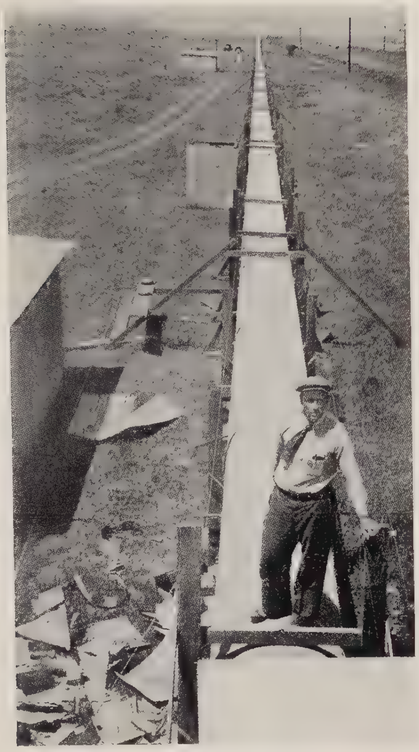
In the Polish paper *Illustracja Polska*, No. 38, there appears the illustration here reproduced of this latest apparatus, showing the evacuated tube traversed by the beam of light. The control room of the apparatus is shown also. While actually working on these instruments Michelson had a sudden fainting fit. Immediately he regained consciousness, he asked what were the results of the experiment, and those were his last words.

Of Michelson's personality something may be added. "What he set out to do he accomplished with a minimum of effort because added to rare ability he had remarkable powers of concentration. Anything with which he was occupied so completely absorbed him that he thought of nothing else. His unusual concentration enabled him to drop whatever he was doing, engage in some other activity, and return to his original task. After several hours in his laboratory, he might play a game of chess or a few sets of tennis, forgetting entirely his experiments. But his companion in the recreation, walking toward his laboratory with Professor Michelson, would find that the game had absolutely passed from his mind, and that he was again absorbed in planning his investigation. Because of his concentration, he always had leisure to do everything that interested him, but he enjoyed only those activities in which he could participate.

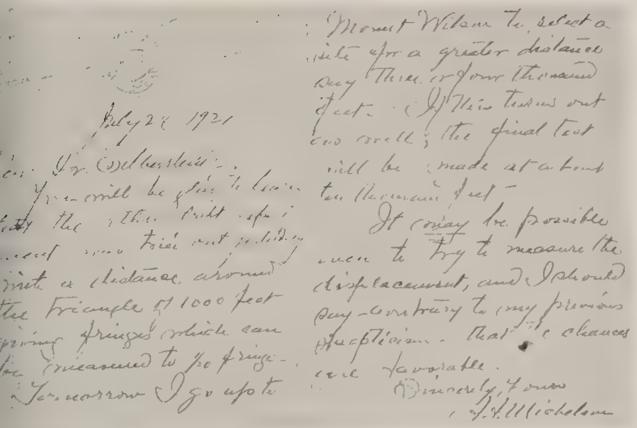
"He preferred to play the violin rather than to attend concerts: he expressed his interest in art by sketching and painting rather than by attending exhibitions. With no patience for mediocrity, whatever he decided to do he wanted to do well, and he would set himself to acquire the necessary technique. When he first came to the University of Chicago he was an indifferent billiard player, but because that game was one of the few diversions at the Quadrangle Club in which he could join his associates, he practised assiduously until he was proficient. More than thirty years ago, when he was nearly fifty years of age, he decided to improve his tennis game, and with the same determination with which he worked on an experiment, he practised strokes.

"In bridge he was not proficient, because he never set himself to master it. One reason, perhaps, was that his memory was of the 'long type'—he could remember every move of chessmen in a game played a year before, but he could not remember cards he had just played. When he was in the navy he was ordered to participate in a topographic survey for planning coast defences. In the mechanics of warfare he

Prof. A. A. MICHELSON.



Exterior of apparatus for determining the velocity of light.



July 28 1921

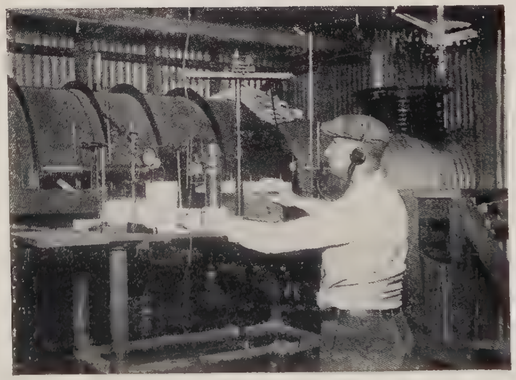
Dr. Silberstein:

You will be glad to learn
that the ether drift exp
ment was tried out yesterday
with a distance around
the triangle of 1000 feet
ving fringes which can
be measured to 1/20 fringe.
Tomorrow I go up to
Mount Wilson to select a
site for a greater distance
say three or four thousand
feet. If this turns out
so well, the final test
will be made at about
ten thousand feet.

It may be possible
even to try to measure the
displacement, and I should
say – contrary to my previous
scepticism – that the chances
are favorable.

Sincerely Yours
A. A. Michelson

Letter to Dr Silberstein.



Control room of apparatus for determining the velocity of light.

was not interested, and though his maps were beautifully accurate, he incurred the censure of his superiors because the borders were illustrated with pictures he had sketched of scenes that had caught his eye.

"His intense interests were satisfied without the development of any eccentricities. Something of the navy tradition remained with him throughout his life, reflected in his meticulous regard for his appearance and his punctilious observance of social form. In Ryerson Laboratory, associates recall, he was a little the admiral on the quarterdeck, courteously formal, the officer in command. No one ever saw him hurried or anxious, nor heard him raise his voice.

"Absolute honesty, the kindliest of courtesy, simplicity, and rigid self-control were his predominating personal qualities. Cordial and kindly to everyone, he had few intimate friends. Even these he did not call by their first names, for the discipline of his early career had given him a formality that was tempered only by his serenity and kindliness. He had, however, a deep feeling for those upon whom he bestowed affection, and would drop any task to spend a few minutes with his grandchildren.

"Whatever of vanity he had was early suppressed: whatever realization he had of his greatness and secure position in the history of civilization was never apparent. He could be brought to talk of his experiments only by direct questioning, and then he told the facts simply and impersonally. He had, though few even of his associates ever knew so, opinions and views on many questions and personalities, but he did not make them public property. He was a lifelong sufferer from insomnia, averaging in the last decade of his life less than five hours' sleep a night, but it never occurred to him to talk of the fact nor to discuss any other phases of his private life.

"He was self-contained to the point of being self-effacing, not through pride nor desire to be secretive, but wholly because he could not conceive of any interest in himself. When he came into the Quadrangle Club for lunch, he would take a seat by himself, but should any of his colleagues care to join the scientist he was quietly welcomed. He was one of the most inconspicuous figures on the campus. To those who asked, he would show his sketches and paintings, but visitors learned not to admire them openly, for Professor Michelson would insist on his guest accepting as a gift any work that was praised.

"He had a highly developed aesthetic sense, which found expression not only in his painting and composition of music, but in other more unusual forms. Twenty years ago, on a trip to South America, he found a species of beetle with bright and beautiful colours. Thinking they might please his children, he collected a group of them. On shipboard, his active mind began considering the physical causes of the brilliant coloration, and the speculation opened up a minor scientific problem that amused him for nearly ten years. He examined beetles, humming birds, moths and butterflies, figuring angles of incidence and other formulae, until he reached a definite conclusion. Incidentally, that diversion produced a spirited scientific debate with a celebrated English physicist, who did not agree with his conclusions. Professor Michelson had a deep philosophical interest and was a member of the American Philosophical Society, the organization founded by Benjamin Franklin. For years he attended its annual meetings in Philadelphia, greatly enjoying the contact with thinkers in fields other than his. He knew many modern languages, and one of his milder diversions took the form of wide reading in Spanish and Italian literature(16)."

The following further notes on his personality are derived from two who knew him(17).

"Michelson dealt with facts without regard to whether they corresponded to his preconceptions or not, and, in fact, invariably attempted to avoid preconceptions of any kind. While he had a good knowledge of analysis, he was not interested particularly to follow the physical implications of the work he did. In his apparatus he frequently designed very simple and ingenious ways of doing things in which the temptation might be to do them in a more complicated manner. He was a good athlete, and was interested in sports, particularly tennis, throughout his life. Millikan mentioned that in playing tennis with him it was interesting to note that his calls were absolutely precise: he never gave either his opponent or himself the advantage of a doubt—indeed, he never seemed to have a doubt. When a ball was out, he said 'out,' and when it was in, he said 'in.' He was very positive in his views, and upheld them vigorously. He was not a teacher, except to those who were doing research with him: and indeed did not enjoy having students to work with him, considering that one of two things happened. If the student was poor, he was in the way: if he was good, he thought that the work was his and not Michelson's. He was a spasmodic rather than a steady worker, working at high speed when he was interested, and his output of work might seem to one near him not to be great." How impressive that work becomes when viewed from afar we all know, and this is doubtless because his achievements, though small in number, were all singularly complete and perfect in conception and execution, and all of them were of the very first importance. Perhaps only the most difficult problems fully aroused his genius.

"He was excellent company, bright and jovial, taking a lively part in the conversation, delighted to hear and to tell a good joke. He rather avoided scientific conversation, except in general enthusiastic terms, or concerning some particularly intricate technical difficulties of an experiment which he had just succeeded in conquering. He did not sympathize very much with relativity, and, publicly, scarcely ever alluded to that theory: yet he was not diffident of it: on the contrary, he seemed to attribute to relativity some uncanny power of predicting phenomena which were all verified. He liked a good vigorous walk in mild weather or in a biting frost, though he was equally alert in the scorching heat which is often experienced in Chicago, and he delighted in touring excursions, and spoke with enthusiasm of the beauty of the desert of Arizona where he toured extensively. He was, even at 70, one of the best tennis players in the university circles of Chicago, and an excellent billiard-player. Once, on a very hot afternoon, he played tennis with an opponent under the very hard self-imposed condition that his points should not count unless forming a suite of 5, and he won after some two hours. Before the play was ended a fellow professor came to remind him of a promise to play with him. "Well,' said Michelson, 'let me finish this, then I shall gladly play with you': which he did, vigorously and victoriously, and all this at some 90 or 95° F."

Of honours there is a long list. The chief was the Nobel Prize in 1907, which he was the first American to receive for science. In the same year he received the Copley Medal of the Royal Society, of which he was a foreign member. He was a corresponding member of the British Association, a Fellow and Gold Medallist of the Royal Astronomical Society, an honorary member of the Royal Institution and the Cambridge Philosophical Society, and an honorary or corresponding member of various other learned societies in America and other countries. He was a past president of the American Physical Society and of the American Association for the Advancement of Science, and Exchange Professor at Göttingen in 1911 and at the University of Paris in 1920. Honorary degrees were conferred on him by Cambridge, Yale, Pennsylvania, Leipzig, Göttingen, Christiania, Paris and McGill Universities. He married, in 1899, Edna Stanton of Lake Forest, Illinois, and had one son and three daughters.

As portrayed in the sources of information which I have consulted I have found the character of Michelson rather enigmatical. With all his varied activities, wide circle of acquaintances, and ready acceptance of good company, the man himself in his inmost being seems to have held aloof from any real intimacies. On this account I think it worth while concluding this notice by Michelson's statement of how he himself felt about his work.

"It has happened more frequently than might have been expected that research in pure science has resulted in tremendous industrial developments, as in the case of the researches of Faraday, Maxwell, and Hertz, which laid the foundation for all of our immense organization of electric light and power: telegraph, telephone, wireless, and other applications of electricity and magnetism.

"But quite apart from such direct benefits to humanity, it seems to me that scientific research should be regarded as a painter regards his art, a poet his poems, a composer his music. It would be quite as unfair to ask of these an apology for their efforts; and the kind of benefit which I should most appreciate from research in pure science is much more allied to such non-material results—results which help to increase the pleasure to us all of matter-of-fact existence, and which help to teach man his true relation to his surroundings—his place in Nature."

So the man whose experiments had such unforeseen and impressive results prized them rather as works of art in themselves. The passage reveals, I think, rare serenity and balance of mind.

F. TWYMAN

REFERENCES

(1) *Phil. Mag.* **151**, 449 (1887).

(2) *Nature*, **117**, 1 (1926).

(3) Obituary notice in *Illustracja Polska*, No. 38; *The Times*; and a biographical sketch issued by the Department of Public Relations, the University of Chicago.

(4) *Phil. Mag.* **151**, 463 (1887).

(5) *Nature*, **20**, 99 (1879).

(6) *Trav. et Mém. du Bur. Intern. des Poids et Mesures*, **12**, 1 (1895).

(7) *Astrophys. J.* **61**, 137 (1925).

(8) *Ann. d. Phys.* **17**, 891 (1905).

(9) *Trav. et Mém. du Bur. Intern. des Poids et Mesures*, **12**, 1 (1895).

(10) *Phil Mag.* **30**, 1 (1890).

(11) *Astrophys. J.* **51**, 257 (1920).

(12) *Ibid.* **8**, 37 (1898).

(13) *Ibid.* **65**, 1 (1927).

(14) *Proc. Phys. Soc.* **33**, 275 (1921).

(15) *Astrophys. J.* (1925).

(16) *Personality sketch from the Department of Public Relations, University of Chicago.*

(17) Professor Millikan (communicated to the writer of the notice by one of the audience who heard his obituary address on Michelson in Pasadena) and Dr L. Silberstein, who came in touch with Michelson by suggesting to him the experiment carried out in 1921 on the possible effect of the rotation of the earth in producing an effect on the velocity of light.

MR HERBERT TOMLINSON, F.R.S.

The death of Mr Herbert Tomlinson on June 12, 1931, will recall to the minds of many of our older physicists the nature of the research work done in the later Victorian years. He was born in 1845 and went to St Peter's School, York, from which he gained a scholarship at Christ Church, Oxford. There he studied mathematics and physics, receiving the B.A. degree in 1868.

Shortly after graduation he went as demonstrator and lecturer in physics to King's College, London, under Professor Grylls Adams. It will be remembered that Clerk Maxwell, the centenary of whose birth is being commemorated in October, was professor of physics at King's College from 1860–65, and he had made the laboratory a centre of research. When he resigned, Professor Grylls Adams, brother of the discoverer of the planet Neptune, was appointed, and Mr Tomlinson on coming into this genial and intellectual atmosphere soon had his mind turned to research. The present writer, in looking over the subjects of Mr Tomlinson's papers, feels that he can trace the influence of Maxwell in the problems and methods used in them. The viscosity of air is one of the subjects that attracted Tomlinson. Maxwell had made measurements with oscillating plates; Tomlinson used spheres attached to a rod which was arranged to oscillate at the end of a torsion wire. Sir George Stokes, then president of the Royal Society, was interested in the experiment and calculated a correction for the rotational effect of the spheres, and indeed communicated the paper to the Society. It is interesting to compare the final result, 0·00017711 at 11°·79 C., with the recent determination by the capillary-tube method made by Professor Rankine who found 0·0001770 at 11°·2 C. and 0·0001803 at 15°·5 C.

Many of Tomlinson's other papers, most of which were communicated to the Royal Society by Professor Grylls Adams, dealt with the internal friction of metals and the effects of temperature and magnetism on this friction, and with the velocity of sound in wires determined directly and indirectly. These subjects formed the matter of many extensive papers in the Royal Society's *Transactions*, and for his work he was elected a Fellow on June 6, 1889. Among the others elected at the same meeting were John Aitken, Horace T. Brown, Latimer Clark, Professor McKenny Hughes and Professor Sollas.

Tomlinson joined the Physical Society in its first session, and the 1926 list contains the name of only one other who joined that session. He was a life member, and served on the Council.

In 1894 Tomlinson gave up the work at King's College for the post of Principal of the newly built South-western Polytechnic at Chelsea, and this work in technical education absorbed his activity until 1904. Among the many classes that he instituted was a Saturday morning class for team-work in research. He and a number of the more advanced students met for the purpose of a united attack on some problem in elasticity or magnetism. The results were difficult to utilize, for although he was an experienced research-worker himself, his assistants could claim but little facility at practical work.

In 1904 he resigned the principalship and retired to Bexhill, where he devoted much time to wireless telegraphy, then in its infancy. It was characteristic of him that when he left London he told the present writer that he would never revisit it; and so far as the writer knows he kept his word. Unfortunate circumstances deprived him of his small fortune, and as he was ineligible for any educational pension he received a Civil List pension for his scientific work. During the War he served for some time as a science teacher at Lancing College.

Tomlinson was a man of intense devotion to a task that interested him, but he had also the capacity of putting aside a subject and taking up another with equal intensity. He was a most pleasant and cordial principal and received the devotion of his staff and students. His intimate friends included the late Professor Reinold, but he was not known to many of the younger school of physicists. His work was of importance in tracing changes in the properties of matter under varying conditions, and he brought to general notice many of these properties which in his time were little appreciated.

S. SKINNER

REVIEWS OF BOOKS

An Introduction to Applied Optics, Vol. 1, *General and Physiological*, by L. C. Martin, D.Sc., A.R.C.S., D.I.C. Pp. ix + 324. (London: Sir Isaac Pitman and Sons, Ltd., 1930.) 21*s*.

In general our text-books can easily be divided into two categories. The material of a new text-book of one class can be practically all found in two or three of its predecessors, and very often the errors of an earlier text are repeated in the new. Unfortunately this class is by far the more numerous, since the writing of such text-books involves a minimum expenditure of time and effort. It is this class of writing that is responsible for the common complaint that new and important material does not "get into the text-books" for ten or more years. Occasionally, however, we are rewarded with a book of the other class, which presents the subject from a fresh viewpoint. It is usually written by one who has specialized in the subject for many years, and therefore contains much material that has never found its way into the stereotyped class book.

Dr Martin's book is clearly of this latter class and he is to be congratulated on achieving so much in the almost superhuman task of giving a fair *résumé* of present day applied optics. The elementary theory given in the first chapter includes Dowell's new graphical construction for tracing a ray through an optical system, and a numerical example of trigonometric tracing as used in lens designing. Chapter 2 deals with the general theory of optical systems both graphically and analytically. In the third chapter, just enough physical optics is introduced to enable the reader to understand the nature of the diffractional effects obtained with telescopes, and the chief methods of investigating the properties of radiation are briefly summarized. The fourth chapter is a masterly account of the defects of optical images. This is probably unequalled in any other book, and no serious student of optics should miss the clear account of aberration that is given here. Chapter 5 deals with the eye and physiological optics and is followed by further chapters on physical optics, optical glass (including lens-polishing) and spectacles.

The book is singularly free from misprints, but one occurs on p. 184. The phase-change on reflection at a denser medium is an *advance* of π, so that the minus sign should be used in the expression for the total path-difference. The text for striae given on p. 241 is very much improved when the eye is placed behind an obstacle slightly larger than the image of the small light-source that falls on it. These are very minor points, and the book can be whole-heartedly recommended to all who are interested in practical optics and to those who wish to make the most of the optical instruments that they use as tools. The appearance of the second volume, dealing with the telescope and the microscope, will be awaited with interest.

W. E. W.

The Scientific Journal of the Royal College of Science, Vol. 1. Pp. 158. (London: Imperial College Union, 1931.) 3*s*.

With the rapid growth of the sciences comes a growing need for accounts which, while sufficiently elementary to appeal to students not specially versed in the details of the science dealt with, are yet technical enough to be of interest to the expert. It is not easy to find such accounts; the difficulties are patent and well-known –they are in fact the difficulties that face every one whose lot it has been to contribute an article to an encyclopædia. But addresses given before student societies are as likely as not to hit the mark, and, to whomsoever be the credit, it was a happy thought to induce three of the student societies of the Imperial College to join forces. The result has been the production of a volume of permanent interest. The three societies concerned are the Imperial College Chemical Society, the R.C.S. Natural History Society, and the R.C.S. Mathematical and Physical Society. The first-named society is not new to the business—it has for nine years past produced an annual journal. The present volume continues worthily the traditions of its predecessors and contains five authoritative addresses by W. H. Perkin, on high-pressure chemical plant, on the mechanism of the combination of hydrogen and oxygen, and on the polymerizing capacities of unsaturated compounds. This in itself is good enough fare, but the volume is greatly strengthened by the addition of three natural history lectures on the Alps, on plant-breeding, and on tree crops, and of four lectures—on moving magnetic fields, time, the determation of gases and the nature of vowel and consonant sounds—which were delivered before the Physical and Mathematical Societies.

The societies concerned are to be heartily congratulated on their venture; their first volume is pleasant to look at and to handle and good to read, and we trust that it will be the ancestor of a long and healthy line. A. F.

A Survey of Physics (*for College Students*), by Prof. F. A. SAUNDERS. Pp. x + 635. (London: G. Bell and Sons, Ltd.) 14*s*.

The chief virtues of this book lie in its modern viewpoint and its thoroughly practical outlook. Among other things, it gives brief accounts of or mentions series spectra, the Schottky effect, the Raman effect, wave mechanics, electron-diffraction and relativity. While no very obvious immediate purpose is served by brief non-mathematical accounts of some of these, there is much to be said for introducing some mention of them at an early stage in physics courses.

The book is good on the practical side, and it freely mentions modern technical applications. The exercises and problems are generally so devised as to give sound ideas on common physical magnitudes rather than mere practice in arithmetical manipulation. The practical outlook and general style may be illustrated by quotation from a passage (p. 21) which accompanies a highly moral tale of the discomfiture of an inventor who lacked instruction in the elements of theoretical physics: "It makes an instructive illustration of the magnitude of the air pressure to exhaust the air from the inside of an old tin can, provided that it is no longer needed." This might have been less ambiguously expressed, but it would be difficult to devise a mode of exposition more likely to drive the lesson home.

On the systematic and theoretical side the treatment is less adequate—less so than that of many established texts of similar range. It is at times even a little misleading. For example, the electronic change is deduced (p. 363) by dividing $6{\cdot}06 \times 10^{23}$ (Avogadro's number per gramme-molecule) into Faraday's constant, and stress is laid upon the exactitude of the agreement of this result with Millikan's oil-drop value. It is surely a little disingenuous to suggest that this particular agreement proves anything beyond the reliability of the ordinary rules of arithmetic.

In spite of defects of this kind, the book is clearly and vigorously written, and most junior students of physics could read it with both profit and pleasure. It contains many things which are not to be found in the more conventional elementary texts, and some excellent photographs.

It should be pointed out (after the announcement on the dust-cover) that the book provides only a *preliminary* "survey of all the general physics demanded... by a pass degree examination." The text and the many excellent problems and exercises are in the main of a standard not very different from those associated with work for intermediate science, pre-medical and school-certificate examinations in this country. H. R. R.

Thermodynamics, by ALFRED W. PORTER, D.Sc., F.R.S. Fcap. 8vo, pp. vii + 96. (London: Methuen, 1931.) 2*s* 6*d*.

The number of possible solutions of the problem of selection of material for a small book on thermodynamics must be very large. The one embodied in this work seems thoroughly suited for a third-year course for students reading for an honours degree. After an historical introduction of 20 pages, which commences with the foundations of mechanics, it deals in succession with reversible changes and their applications, with irreversible changes and with equilibrium. The treatment of gas equations is particularly good and will give a student a much clearer idea of their limitations than he can obtain from many larger works. There are few misprints (pp. 36, 37), but the absence of numbering from the equations is an inconvenience when "it has been shewn that" is encountered.

C. H. L.

Krieselräder als Pumpen und Turbinen, Vol. 1, by WILHELM SPANNHAKE, Professor at the Karlsruhe Technical High School. 8vo, pp. viii + 320. (Berlin: Springer, 1931.) 29 marks.

In this volume, which is the first of what promises to be an extensive treatise, the author establishes the hydrodynamical theorems applicable to machines and plant which deal with the flow of fluids. Turbulent motion is not included, but in cases where the one-dimensional stream-line theory, which is the principal feature of the book, is found insufficient, corrections, such as experience has shewn to be necessary, are applied to the velocities and energies. This enables an outline of the subject to be traced, which the second volume will fill in and render more exact, while the third volume will deal with the mechanical details of the machines. The volume is well printed and illustrated.

C. H. L

Meteorological Office, Professional Notes. No. 52: *Bumpiness on the Cairo-Basra Air Route*, by J. DURWARD, M.A. 8vo, pp. 6. (London: H.M. Stationery Office, 1929.) 3*d*.

The rises and falls of an aircraft due to vertical air currents, which are brought about generally by irregular country, are least in the early morning, but may at other times be experienced at altitudes of 12,000 feet.

C. H. L.

Meteorological Office, Professional Notes. No. 53: *The Relation between the Duration of Bright Sunshine and the Amount of Cloud*, by C. E. P. BROOKS, D.Sc. 8vo, pp. 15. (London: H.M. Stationery Office, 1929.) 9*d*. net.

By comparing the records of Campbell-Stokes sunshine-recorders with those of cloudiness, the author has deduced a formula giving the duration of bright sunshine in terms of cloudiness which allows the sunshine to be calculated from observations of clouds, made at three or more periods of the day, at places where sunshine recorders are not available.

C. H. L.

Meteorological Office Réseau Mondial 1924. 4to, pp. xv – 115. (London: H.M. Stationery Office, 1931.) 25*s.* net.

No change has been made in the form of publication of this volume as compared with that of the previous year.* The number of stations utilized was 479 for the year, as against 463 for the previous year. C. H. L

Meteorological Office, Geophysical Memoirs. No. 48: *The Meteorological Results of Journeys in the Southern Sahara*, 1922 and 1927. Made by F. R. Rodd, F.R.G.S. Discussed by C. E. P. Brooks, D.Sc. and S. T. A. Mirrlees, M.A. 4to, pp. 40. (London: H.M. Stationery Office, 1929.) 3*s.* 6*d.* net.

The region north of Kano (12° N. to 20° N.) has a winter dry season with north-easterly winds and a summer wet season with south-westerly winds and a rainfall of 34 inches at Kano, considerably less to the north, and in the northern plains probably less than 5 inches. In summer the nights are warm and oppressive. C. H. L.

Meteorological Office, Geophysical Memoirs. No. 49: *Two Notes on the Operation of Galitzin Seismographs*, by F. J. Scrase, M.A., B.Sc. Pp. 9. (London: H.M. Stationery Office, 1930.) 1*s.* net.

A diagram is given enabling the damping-constant and the free period of a Galitzin seismograph to be readily evaluated. The variation of the period of the pendulum with position, brought about by the single control spring, can be overcome only by the use of additional springs. C. H. L.

Meteorological Office, Geophysical Memoirs. No. 52: *Some Characteristics of Eddy Motion in the Atmosphere*, by F. J. Scrase, M.A., B.Sc. Pp. 16. (London: H.M. Stationery Office, 1930.) 1*s.* 6*d.* net.

The eddy motions in the wind over Salisbury Plain have been studied by means of kinematograph records of the position of a wind-vane free to move both horizontally and vertically, and of a Dines anemometer. For average eddy motion the eddy speeds across and down the wind are proportional to the mean wind speed, the horizontal cross-wind speed being greater than the down-wind speed, and that greater than the vertical speed. The ratios of these speeds vary with height above the ground. C. H. L.

Novius Organum, by James Clark McKerrow, M.B. Pp. viii 277. (London: Longmans Green and Co. Ltd., 1931.) 9*s.*

Mr McKerrow's title is well chosen; his philosophy is in the classical tradition, even if his exposition of it is not in the classical style. For he will explain the universe to us, whether under the aspect of cosmogony or of social economics, in terms of a single principle—the principle of "habit," which makes things repeat their activity.

The only question that need be asked here is whether Mr McKerrow's arguments, often acute and entertaining, are of particular interest to physicists. The answer is that they are not. The "limited, second-hand, and popular knowledge" to which he confesses, does not necessarily make his "liberty of thought border on licence"; but a philosopher who appeals to scientists must take the scientific attitude towards science and refrain from criticizing theories on the ground that they fail to solve problems lying entirely outside their range. N. R. C.

---

* *Proc. Phys. Soc.* **43**, 118 (1931).

INDEX TO VOLUME 43

PAGE

Absorption and dissociative or ionizing effect of monochromatic radiation in an atmosphere on a rotating earth 26, 483
Andrade, E. N. da C., and Smith, D. H.: Formation of sand figures on a vibrating plate 405
Andrews, J. P.: A simple approximate theory of the pressure between two bodies in contact 1
Andrews, J. P.: Experiments on impact 8
Andrews, J. P.: Observations on percussion figures 18
Annual Exhibition of the Physical and Optical Societies: opening address by President 119
Antimony, The spectra of trebly and quadruply ionized 538
Argon, Displacements in the spectrum of ionized 279
Arsenic, The spectrum of doubly ionized 68
Atmosphere on a rotating earth, The absorption and dissociative or ionizing effect of monochromatic radiation in an 26, 483
Atmospheric ozone, A photoelectric spectrophotometer for measuring the amount of 324
Attenuation of ultra-short radio waves due to the resistance of the earth . . 592
Awbery, J. H., *see* Sherratt, G. G.

Badami, J. S.: The spectra of trebly and quadruply ionized antimony . . 538
Badami, J. S.: The spectrum of trebly ionized cerium 53
Ballistic recorder for small electric currents 254
Barium fluoride, The spectrum of 554
Bates, L. F.: The Curie points 87
Beckett, H. E.: The reflecting powers of rough surfaces at solar wave-lengths . 227
Bond, W. N.: Magnetostriction and hysteresis 569
Bond, W. N.: Turbulent flow through tubes 46
Books, Reviews of 113, 219, 364, 458, 635
Bowker, H. C.: Variation of spark-potential with temperature in gases . . 96
Bridges, Precision condenser 564
Bryan, G. B.: Demonstration of some stroboscopic effects 218
Butterworth, S. and Smith, F. D.: The equivalent circuit of the magnetostriction oscillator 166

Callendar, H. L., Obituary notice of 620
Campbell, A.: Precision condenser bridges 564
Cathode-ray oscillography of irregularly recurring phenomena, A time base for the 502
Cerium, The spectrum of trebly ionized 53
Chapman, S.: The absorption and dissociative or ionizing effect of monochromatic radiation in an atmosphere on a rotating earth 26, 483
Chloroform, The refraction and dispersion of gaseous 559
Cohesion 461

PAGE

Combining two curves into one, Demonstration of an instrument for . . . 112
Condenser bridges, Precision 564
Conductivity, Thermal, and its temperature-variation for medium conductors . 581
Crystallograph, The Hilger X-ray 512
Crystal-orientation of the cathode, The influence of, on that of an electro-deposited layer 138
Cubic-crystal analyser 512
Curie points 87
Current pulses of rectangular wave-form, The generation of 371
Currents, A ballistic recorder for small electric 254

Diffusion effect, thermal, The influence of low temperatures on . . . 142
Dobson, G. M. B.: A photoelectric spectrophotometer for measuring the amount of atmospheric ozone 324
Duddell Medal, Presentation of, to Sir J. A. Fleming 613

Eddington, A. S.: Opening address by President at the Physical and Optical Societies' Annual Exhibition 119
Edge tones 394
Electro-deposited layer, The influence of the crystal-orientation of the cathode on that of an 138
Electro-endosmosis and electrolytic water-transport 524
Electrolytic water-transport, Electro-endosmosis and 524
Elliot, J. K., *see* Lowery, H.
Ensor, C. R.: Thermal conductivity and its temperature-variation for medium conductors 581
Ethyl bromide, The refraction and dispersion of gaseous 562

Fahmy, M.: A point of analogy between the equations of the quantum theory and Maxwell's equations 124
Fereday, R. A.: Comparison of small magnetic susceptibilities 383
Finch, G. I., Sutton, R. W., and Tooke, A. E.: A time base for the cathode-ray oscillography of irregularly recurring phenomena 502
Fleming, Presentation of the Duddell Medal to Sir J. A. 613
Flow through tubes, Turbulent 46

Gamma-rays, The photographic effects of 59
Gauges, Demonstration of plug and ring 217
Glazebrooke, R. T.: Standards of measurement, their history and development (sixteenth Guthrie lecture) 412
Grew, K. E., *see* Ibbs, T. L.
Guthrie Lecture, The sixteenth 412

Hartley, T. S., *see* Lowery, H.
Hase, R.: Some studies in pyrometry and on the radiation properties of heated metals 212
Haughton, J. L.: Demonstration of an instrument for combining two curves into one 112
Henry, P. S. H.: The tube effect in sound-velocity measurements 340

PAGE
Hepburn, H. C.: Electro-endosmosis and electrolytic water-transport . . 524
Hot-wire microphones, The determination of the acoustical characteristics of singly-resonant 72

Ibbs, T. L. and Grew, K. E.: The influence of low temperatures on the thermal diffusion effect 142
Illumination for ultra-violet microscopy, Sources of 127
Impact, Experiments on 8
Iron, Note on the elimination of the β wave-length from the characteristic radiation of 275
Irons, E. J.: Demonstration of some elementary experiments concerned with sound-waves in tubes 363

Johnson, B. K.: Sources of illumination for ultra-violet microscopy . . . 127

Lang, H. R.: On the measurement of the total heat of a liquid by the continuous mixture method 572
Lennard-Jones, J. E.: Cohesion 461
Lowery, H. and Elliot, J. K.: The refraction and dispersion of gaseous ethyl bromide 562
Lowery, H. and Hartley, T. S.: The refraction and dispersion of gaseous pentane and chloroform 559

Maddock, A. J.: The generation of current pulses of rectangular wave-form . 371
Magnetic susceptibilities, Comparison of small 383
Magnetostriction and hysteresis 569
Magnetostriction oscillator, The equivalent circuit of the 166
Magnetostrictive oscillators at radio-frequencies, Experiments on . . . 157
Martin, L. C.: The theory of the microscope 186
Maxwell's equations, A point of analogy between the equations of the quantum theory and 124
McPetrie, J. S., *see* Smith-Rose, R. L.
Mercury, The high-frequency spectrum of 545
Michelson, Prof. A. A., Obituary notice of 625
Microphones, The determination of the acoustical characteristics of singly-resonant hot-wire 72
Microscope, The theory of the 186
Mixture method, On the measurement of the total heat of a liquid by the continuous 572
Moss, E. B.: A ballistic recorder for small electric currents 254

Neon, Displacements in the spectrum of ionized 279
Nevin, Thomas E.: The spectrum of barium fluoride 554

Oscillators, magnetostrictive, at radio-frequencies, Experiments on . . . 157
Oscillography of irregularly recurring phenomena, A time base for the cathode-ray 502
Oxygen, Displacements in the spectrum of ionized 279
Ozone, atmospheric, A photoelectric spectrophotometer for measuring the amount of 324

PAGE

Paris, E. T.: The determination of the acoustical characteristics of singly-resonant hot-wire microphones 72
Pentane, The refraction and dispersion of gaseous 559
Percussion figures, Observations on 18
Phase-difference of seismograph records, The instrumental 259
Pressure between two bodies in contact, A simple approximate theory of the . 1
Pretty, W. E.: Displacements in the spectra of ionized oxygen, neon and argon . 279
Pyrometry, Some studies in 212

Quantum theory and Maxwell's equations, A point of analogy between the equations of 124

Radiation in an atmosphere on a rotating earth, The absorption and dissociative or ionizing effect of monochromatic 26, 483
Radiation of iron, Note on the elimination of the β wave-length from the characteristic 275
Radiation properties of heated metals, Some studies on the 212
Radio waves, The attenuation of ultra-short, due to the resistance of the earth . 592
Rao, K. R.: The spectrum of doubly ionized arsenic 68
Reflecting powers of rough surfaces at solar wave-lengths 227
Refraction and dispersion of gaseous ethyl bromide 562
Refraction and dispersion of gaseous pentane and chloroform 559
Resistivity method of geophysical surveying, The earth 305
Reviews of books 113, 219, 364, 458, 635
Richardson, E. G.: Edge tones 394
Rogers, J. S.: The photographic effects of Gamma-rays 59
Rolt, F. H.: Demonstration of plug and ring gauges 217
Rough surfaces, The reflecting powers of, at solar wave-lengths 227

Sand figures on a vibrating plate, Formation of 405
Scrase, F. J.: The instrumental phase-difference of seismograph records . . 259
Seismograph records, The instrumental phase-difference of 259
Sherratt, G. G. and Awbery, J. H.: The velocity of sound-waves in a tube . 242
Smith, D. H., *see* Andrade, E. N. da C.
Smith, F. D., *see* Butterworth, S.
Smith-Rose, R. L. and McPetrie, J. S.: The attenuation of ultra-short radio waves due to the resistance of the earth 592
Sound-velocity measurements, The tube effect in 340
Sound-waves in a tube, The velocity of 242
Sound-waves in tubes, Demonstration of some elementary experiments concerned with 363
Spark-potential, Variation of, with temperature in gases 96
Spectra of ionized oxygen, neon and argon, Displacements in the 279
Spectra of trebly and quadruply ionized antimony, The 538
Spectrophotometer for measuring the amount of atmospheric ozone, A photo-electric 324
Spectrum of barium fluoride 554

PAGE
Spectrum of doubly ionized arsenic 68
Spectrum of mercury, The high-frequency 545
Spectrum of trebly ionized cerium 53
Standards of measurement, their history and development 412
Stroboscopic effects, Demonstration of some 218
Surveying, The earth-resistivity method of geophysical 305
Sutton, R. W., *see* Finch, G. I.

Tagg, G. F.: The earth-resistivity method of geophysical surveying . . . 305
Thermal conductivity and its temperature-variation for medium conductors . 581
Thermal diffusion effect, The influence of low temperatures on the . . . 142
Time base for the cathode-ray oscillography of irregularly recurring phenomena 502
Tolansky, S.: The high-frequency spectrum of mercury 545
Tomlinson, Obituary notice of Dr H. 633
Tooke, A. E., *see* Finch, G. I.
Total heat of a liquid by the continuous mixture method, Measurement of the . 572
Turbulent flow through tubes 46

Ultra-violet microscopy, Sources of illumination for 127

Velocity of sound-waves in a tube 242
Vibrating plate, Formation of sand figures on a 405
Vincent, J. H.: Experiments on magnetostrictive oscillators at radio-frequencies 157

Water-transport, Electro-endosmosis and electrolytic 524
Wave-form, The generation of current pulses of rectangular 371
Wood, W. A.: Note on the elimination of the β wave-length from the characteristic
    radiation of iron 275
Wood, W. A.: The influence of the crystal-orientation of the cathode on that of an
    electro-deposited layer 138

Zeidenfeld, S.: The Hilger X-ray crystallograph and the cubic-crystal analyser . 512

CAMBRIDGE: PRINTED BY
W. LEWIS, M.A.
AT THE UNIVERSITY PRESS

PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1930–31

Except where the contrary is stated, the meetings were held at the Imperial College of Science and Technology, South Kensington.

October 17, 1930.

Mr R. W. Paul in the Chair.

1. The President announced that the Council had elected R. A. Newing, G. D. Pegler, Wilfred Pagley, Donovan Chilton, Hilda E. Carpenter, Elsie A. Simmons, Edith Dora Vedy, Charles John Birkett Clews to be Student Members of the Society.

2. A paper entitled "A simple approximate theory of the pressure between two bodies in contact," was read by J. P. Andrews, M.Sc., F.Inst.P.

3. A paper entitled "Experiments on impact," was read by J. P. Andrews, M.Sc., F.Inst.P.

4. A paper entitled "Observations on percussion figures," was read by J. P. Andrews, M.Sc., F.Inst.P.

5. A paper entitled "Some physical radiometric investigations of technical interest," was read by Dr Rudolf Hase.

November 7, 1930.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. Roger Daniel Hewart Jones, Robert Stephen Dadson, George Paget Thomson, Syed Mohamad Ali Khan, Herbert John Gough, Thomas Musgrave Pyke, R. F. Hanstock, R. S. Mani, P. V. Kuruvila, H. R. Robinson, H. Amorim Ferreira, Louis George Melio, Donald Thomas Jones, H. Harrison Macey were elected Fellows of the Physical Society.

The President announced that the Council had elected E. R. F. P. Mendis to be a Fellow of the Physical Society under Article 14, and Allen James Lewis to be a Student Member of the Society.

2. A paper entitled "The absorption and dissociative or ionizing effect of monochromatic radiation in an atmosphere on a rotating earth," was read by Prof. S. Chapman.

3. A paper entitled "Turbulent flow through tubes," was read by W. N. Bond, M.A., D.Sc., F.Inst.P., Lecturer in Physics in the University of Reading.

4. A paper entitled "The spectrum of trebly-ionized cerium (Ce IV)," was read by J. S. BADAMI, Imperial College of Science and Technology.

5. A paper entitled "The photographic effects of gamma-rays," by J. S. ROGERS, B.A., M.Sc., F.Inst.P., Senior Lecturer in Natural Philosophy, University of Melbourne, was read.

November 21, 1930.

Prof. Sir ARTHUR EDDINGTON, M.A., D.Sc., F.R.S., in the Chair.

1. Thomas Eric Banks, Frank Arthur Long, Mark Thompson, Robert C. G. Williams, Charles Seymour Wright, and William Rees Williams were elected Fellows of the Physical Society.

The President announced that the Council had elected F. B. Levetus and James Alfred Conway Student Members of the Society.

2. A paper entitled "The determination of the acoustical characteristics of singly-resonant hot-wire microphones," was read by E. T. PARIS, D.Sc., F.Inst.P.

3. A paper entitled "The spectrum of doubly-ionized arsenic," by K. R. RAO, D.Sc., Madras Government Research Scholar, University of Upsala, was read.

4. A paper entitled "The effect of temperature on spark-potential," was read by H. C. BOWKER, B.Sc. (Eng.), Ph.D., A.K.C.

5. A paper entitled "The Curie points," was read by L. F. BATES, B.Sc., Ph.D., University of London, University College.

6. A demonstration was given of an instrument for compounding curves, designed by J. L. HAUGHTON, D.Sc., The National Physical Laboratory.

December 5, 1930.

Prof. Sir ARTHUR EDDINGTON, M.A., D.Sc., F.R.S., in the Chair.

1. Alan Julian Maddock, John Francis Robertson, Thomas Lidyard Rosgyll Ayres, William Lethersich, Karl Manne Georg Siegbahn, Mary John, Homer L. Dodge, Wilfred Basil Mann, and Leonard Francis Osmond were elected Fellows of the Physical Society.

2. A paper entitled "A point of analogy between the equations of the quantum theory and Maxwell's equations," by M. FAHMY, The Egyptian University, Cairo, was read.

3. A paper entitled "Sources of illumination for ultra-violet microscopy," was read by B. K. JOHNSON, F.R.M.S.

4. A paper entitled "The influence of the crystal-orientation of the cathode on that of an electro-deposited layer," was read by W. A. Wood, M.Sc., National Physical Laboratory.

5. A paper entitled "Relations between the fundamental physical constants," was read by C. A. Kloss, B.Sc., A.I.C., British Electrical and Allied Industries Research Association.

6. A demonstration of some stroboscopic effects was given by Prof. G. B. Bryan, D.Sc., Royal Naval College, Greenwich.

January 6, 7 *and* 8, 1931.

The twenty-first annual exhibition of the Physical Society and the Optical Society was held in the Imperial College of Science.

Discourses were delivered as follows:

January 6th: Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., opening address.

January 7th: E. Lancaster-Jones, B.A., "Searching for minerals with scientific instruments."

January 8th: Prof. Sir Gilbert Walker, F.R.S., "The physics of sport."

January 16, 1931.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. Henry C. Calvert, Claude L. Lyons, Luang Brata, Robert Donaldson, Thomas Arthur Chalmers, William Edward Thomas Perry, Charles Edward Robinson and Clifford Wainwright were elected Fellows of the Physical Society.

The President announced that Robert Welham Haward, Aileen Mary Prior and Walter Wilson had been elected to Student Membership of the Society.

2. A paper entitled "The influence of low temperatures on the thermal diffusion effect," by T. L. Ibbs, M.C., Ph.D. and K. E. Grew, Ph.D., was read by Dr Ibbs.

3. A paper entitled "Further experiments on magnetostriction oscillators at radio frequencies," was read by J. H. Vincent, M.A., D.Sc., F.Inst.P.

4. A paper entitled "The equivalent circuit of the magnetostriction oscillator," by S. Butterworth, M.Sc. and F. D. Smith, M.Sc., A.M.I.E.E., was read by Mr Butterworth.

5. A paper entitled "The theory of the microscope," was read by L. C. Martin, D.Sc., A.R.C.S., D.I.C.

6. A demonstration of plug and ring gauges was given by F. H. Rolt, National Physical Laboratory.

February 6, 1931.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. Robert William Corkling, S. Rama Swamy, Basil Gordon Dickins, and Ernest Gordon Cox were elected Fellows of the Physical Society.

The President announced that Eric George Longhurst, Arthur Joseph Woodall, Ailsa W. Ikin, David Arthur Bell, David Evered Harrell Jones, and Charles Henry Kemp had been admitted to Student Membership of the Society.

2. A paper entitled "The radiation-reflecting powers of rough surfaces," was read by H. E. Beckett, B.Sc.

3. A paper entitled "A ballistic recorder for small electric currents," was read by E. B. Moss, B.Sc.

4. A paper entitled "The instrumental phase-difference of seismograph records; an illustration of the properties of damped oscillatory systems," was read by F. J. Scrase, M.A., B.Sc., Kew Observatory.

February 20, 1931.

Mr J. Guild in the Chair.

1. Mrs Freda Stilwell, James Ronald Clarkson, Raymond George Wood, and Cyril Alfred Sinfield were elected Fellows of the Physical Society.

2. A paper entitled "On the velocity of sound waves in a tube," by G. G. Sherratt, B.A. and J. H. Awbery, B.A., B.Sc., F.Inst.P., Physics Department, National Physical Laboratory, Teddington, Middlesex, was read by Mr Sherratt.

3. A paper entitled "A note on the elimination of the β wave-length from the characteristic radiation of iron," was read by W. A. Wood, M.Sc., Physics Department, National Physical Laboratory.

4. A paper entitled "The tube effect in sound-velocity measurements," was read by P. S. H. Henry, Coutts Trotter Student, the Laboratory of Physical Chemistry, Cambridge.

March 6, 1931.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. Guy Burniston Brown, Thomas Eran Leyshon, Frank Ernest Hoare, Alastair Watson Gillies, and Reginald Frederick Clark were elected Fellows of the Physical Society.

2. A paper entitled "Practical investigations of the earth resistivity method of geophysical surveying," was read by G. F. Tagg, B.Sc., A.M.I.E.E.

3. A paper entitled "A photoelectric spectrophotometer for measuring the amount of atmospheric ozone," was read by G. M. B. Dodson, D.Sc., F.R.S.

4. A paper entitled "Displacements of certain lines of the spectra of ionized oxygen (O II, O III), neon (Ne II) and argon (A II)," was read by W. E. Pretty, B.Sc., A.R.C.S., D.I.C., Assistant Lecturer in Physics, Imperial College, South Kensington.

5. The following experiments and slides were shewn by Eric J. Irons, Ph.D.:

(1) Mechanical lantern slide to demonstrate the formation and properties of stationary waves. The slide consists of two chemically fixed photographic plates upon each of which a sine curve is drawn. Means are provided whereby the curves move in opposite directions and the resultant displacements for various positions of the waves are registered on the board upon which the slide is focussed.

(2) Five lantern slides* illustrating the formation of dust figures in a Kundt's tube excited by a rod.

(3) Determination of the end-correction of a tube. Dust figure gives an ocular demonstration of the fact that an antinode is not formed exactly at the open end of a Kundt's tube and enable an estimate of the end-correction to be made.†

(4) Demonstration of the effect of a Quincke filter on the sound emitted from a valve-maintained tube. If a side branch tuned to a note of particular frequency is fixed in a conduit down which sound waves are passing, the energy associated with that frequency is absorbed in the branch.

Annual General Meeting, March 20, 1931.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. The Minutes of the preceding Annual Meeting were read and confirmed.

2. The Reports of the Council and of the Hon. Treasurer were presented and adopted.

3. Mr J. E. Calthrop and Major W. S. Tucker having been appointed scrutineers, the following officers and members of Council were elected for the year 1931–32:

President: Prof. Sir A. S. Eddington, M.A., D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President): Sir Oliver J. Lodge, D.Sc., LL.D., F.R.S.; Sir Richard Glazebrook, K.C.B., Sc.D., F.R.S.; Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.; Prof. C. Vernon Boys, F.R.S.; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S.; Alexander Russell, M.A., D.Sc., F.R.S.; F. E. Smith, C.B., D.Sc., F.R.S.; Prof. O. W. Richardson, M.A., D.Sc., F.R.S.; W. H. Eccles, D.Sc., F.R.S.

---

* *Phil. Mag.* **7**, 523 (1929).

† *Phil. Mag.* **6**, 580 (1928).

Vice-Presidents: A. B. Wood, D.Sc.; Prof. A. O. Rankine, O.B.E., D.Sc.; J. S. G. Thomas, D.Sc.; J. Guild, A.R.C.S., D.I.C.

Hon. Secretaries: Ezer Griffiths, D.Sc., F.R.S.; Allan Ferguson, M.A., D.Sc.

Hon. Foreign Secretary: Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

Hon. Treasurer: R. S. Whipple, M.I.E.E.

Hon. Librarian: J. H. Brinkworth, M.Sc., A.R.C.S.

Ordinary Members of Council: Lewis Simons, D.Sc.; J. H. Awbery, B.Sc.; T. Smith, M.A.; W. Jevons, D.Sc., D.I.C.; Prof. W. Wilson, Ph.D., D.Sc., F.R.S.; D. Owen, B.A., D.Sc.; B. P. Dudding, M.B.E., A.R.C.S.; Major I. O. Griffith, M.A.; D. W. Dye, D.Sc., F.R.S.; Prof. G. P. Thomson, F.R.S.

4. Votes of thanks to the auditors (proposed by Dr D. Owen and seconded by Dr J. H. Brinkworth), to the retiring officers and Council (proposed by Prof. F. L. Hopwood and seconded by Prof. L. C. Martin), to the Governing Body of the Imperial College of Science and Prof. G. P. Thomson for permission to meet at the College (proposed by Mr T. Smith and seconded by Mr J. Guild) and to the scrutineers (proposed from the Chair) were carried unanimously.

5. The Duddell Medal, 1930, was presented to Prof. Sir J. AMBROSE FLEMING, M.A., D.Sc., F.R.S., a founder Fellow of the Society who read the first paper at the opening meeting of the Society in March 1874. Sir Ambrose Fleming exhibited a collection of apparatus of historical interest.

Prof. H. E. ARMSTRONG, also a founder Fellow, gave a brief address of reminiscence.

April 17, 1931.

Dr J. S. G. THOMAS in the Chair.

1. Ralph Jessel, Sidney Zeidenfeld and Leslie Charles Bailey were elected Fellows of the Physical Society.

The Chairman announced that Miss T. M. Lloyd had been admitted to Student Membership of the Society.

2. A paper entitled "The generation of current-pulses of rectangular waveform," by A. J. MADDOCK, M.Sc., A.Inst.P., was taken as read.

3. A paper entitled "An improved method for the comparison of small magnetic susceptibilities," was read by R. A. FEREDAY, B.Sc., F.Inst.P.

4. A paper entitled "Edge tones," was read (with demonstration) by E. G. RICHARDSON, B.A., Ph.D., D.Sc., University College, London.

May 1, 1931.

Prof. Sir ARTHUR EDDINGTON, M.A., D.Sc., F.R.S., in the Chair.

1. Richard Leonard Ascough Borrow, M. Farrell, R. W. Sutton, Godfrey Henry Barker and Frank Cecil Connelly were elected Fellows of the Physical Society.

2. A lecture was delivered by Prof. J. E. LENNARD-JONES, D.Sc., Ph.D., who took as his subject "Cohesion."

May 15, 1931.

Meeting held at the Science Museum, South Kensington.

Prof. Sir ARTHUR EDDINGTON, M.A., D.Sc., F.R.S., in the Chair.

1. Frank Gill, John Rankine, G. A. Wedgwood, and W. Ewart Williams were elected Fellows of the Physical Society.

The President announced that Denis Raymond Wilson had been admitted to Student Membership of the Society.

2. The Sixteenth Guthrie Lecture was delivered by Sir RICHARD T. GLAZEBROOK, K.C.B., M.A., Sc.D., F.R.S., who took as his subject "Standards of measurement, their history and development."

A vote of thanks to the lecturer was proposed by Sir Frank Smith and seconded by Sir Henry Lyons.

June 5, 1931.

Prof. A. O. RANKINE, O.B.E., D.Sc., in the Chair.

1. Francis Alan Burnett Ward, Sidney J. Kennedy and Sidney Jefferson were elected Fellows of the Physical Society.

2. A paper entitled "Electro-osmosis and electrolytic water-transport," Part 2, was read by H. C. HEPBURN, Ph.D., Birkbeck College.

3. A paper entitled "Spectra of trebly and quadruply ionized antimony, Sb IV and Sb V," by J. S. BADAMI, Imperial College of Science, was read in title.

4. A paper entitled "A time base for the cathode-ray oscillography of irregularly recurring phenomena," by G. I. FINCH, R. W. SUTTON and A. E. TOOKE, Imperial College of Science, was read (with demonstration) by Prof. Finch.

5. A paper entitled "The attenuation of ultra-short radio waves due to the resistance of the earth," by R. L. SMITH-ROSE, D.Sc., Ph.D., A.M.I.E.E. and J. S. MCPETRIE, B.Sc., National Physical Laboratory, was read by Mr McPetrie.

6. A paper entitled "The absorption and dissociative or ionizing effect of monochromatic radiation in an atmosphere on a rotating earth. Part II—Grazing incidence," by S. Chapman, M.A., D.Sc., F.R.S. was read in title.

7. A ripple-tank demonstration of beats as moving interference fringes was given by Mr M. O. Clarke.

June 19, 1931.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., and subsequently
Prof. A. O. Rankine, O.B.E., D.Sc., in the Chair.

A discussion on audition was held.*

The discussion was opened by Dr C. S. Myers, F.R.S. The following also contributed papers:

Dr E. D. Adrian, "The microphonic action of the cochlea in relation to theories of hearing." Dr R. T. Beatty, "Auditory mechanisms." Dr A. W. G. Ewing, "High-frequency deafness." Dr F. Allen, "The perception of intensity of sound in normal, depressed and enhanced states of aural sensitivity." Dr E. G. Richardson, "The dynamical theory of the ear." Sir Richard A. S. Paget, "Audition in relation to speech, and the production of speech sounds by the human vocal apparatus, by acoustic or electrical resonators and by musical instruments." Dr E. W. Scripture, "The nature of the vowels." Dr Erwin Meyer, "The analysis of noises and musical sounds." Prof. E. N. da C. Andrade, "Absolute measurement of sound-amplitudes and intensities." Dr C. V. Drysdale, "Acoustic measuring instruments." Dr H. Banister, "The basis of sound-localization." Dr A. H. Davis, "The measurement of noise." Dr F. Trendelenberg, "Objective measurement and subjective perception of sound." Dr G. Waetzmann and Herr H. Heisig, "The measurement by resonance telephone of the threshold sensitivity of the ear." Major W. S. Tucker, "The localization of sound derived from observations of intensity." Prof. E. M. von Hornbostel, "The time-theory of sound-localization. A re-statement." Mr F. C. Bartlett, "On certain general conditions of auditory measurements."

June 20, 1931.

Meeting held at University College, Reading.

Prof. Sir Arthur Eddington, M.A., D.Sc., F.R.S., in the Chair.

1. A paper entitled "The absorption of X-rays" was read by Prof. J. A. Crowther, M.A., Sc.D.

2. A paper entitled "Magnetostriction and hysteresis" was read by Dr W. N. Bond, M.A.

3. A paper entitled "Radiation from a point source" was read by Mr L. G. Vedy, B.A., B.Sc.

4. After tea a series of seventeen exhibits were shown in the laboratories.

5. The meeting concluded with a trip on the river.

---

* Published in a separate volume.

REPORT OF COUNCIL FOR THE PERIOD ENDING FEBRUARY 28TH, 1931

MEETINGS

During the period covered by the report 12 ordinary science meetings were held at the Imperial College of Science. At these meetings 45 papers were presented and 7 demonstrations given.

On June 4 and 5, 1930, a joint discussion with the Optical Society was held on "Photoelectric cells and their applications," and on June 14, 1930, members of the Society and their friends visited Rugby. In the forenoon they were shown round the research laboratories and works of the British Thomson-Houston Company and were their guests at lunch. In the afternoon the Rugby Radio Station was visited and the party then proceeded to Rugby School where, after tea with the Headmaster and staff, the classrooms and laboratories were inspected under the guidance of Mr F. A. Meier, the Senior Science Master.

A discussion on "Magnetism" was held on May 23, 1930, whilst on October 17, 1930, a lecture was delivered by Dr Rudolf Hase, entitled "Some physical radiometric investigations of technical interest."

EXHIBITION

The twenty-first Annual Exhibition, arranged jointly by the Physical and Optical Societies, was held on January 6, 7 and 8, 1931, through the courtesy of the Governing Body, at the Imperial College of Science. The exhibition was opened by the President of the Physical Society, Sir Arthur S. Eddington, F.R.S., who reviewed the salient points in connexion with the history of the exhibition for the past twenty years. The Research and Experimental Section contained exhibits from 29 sources. Trade exhibits were arranged by 85 firms. Discourses were given by Mr E. Lancaster-Jones on "Searching for minerals with scientific instruments," and by Professor Sir Gilbert Walker, F.R.S., on "Physics of sport."

REPRESENTATIVES ON OTHER BODIES

Dr Ezer Griffiths and Dr A. B. Wood have been nominated as representatives of the Society on the National Committees of the Royal Society, on Physics and Radio-Telegraphy respectively, of the International Unions founded under the International Research Council. Dr Ferguson and Dr D. Owen were appointed as representatives of the Society on the Board of the Institute of Physics, and also on the Science Abstracts Committee. Sir Richard Threlfall represented the Society on the occasion of the jubilee celebrations of the foundation of the Mason Science College and the thirtieth anniversary of the granting of the charter to the University of Birmingham.

THE DUDDELL MEDAL

At the Annual Meeting on March 28, 1930, the seventh (1929) Duddell Medal was presented to Professor A. A. Michelson through the intermediary of the United States Embassy. The Council has awarded the eighth (1930) Duddell Medal to Professor Sir Ambrose Fleming, F.R.S.

GUTHRIE LECTURE

Professor P. Debye delivered the fifteenth Guthrie Lecture on April 11, 1930, the subject being "The scattering of X-rays in gases, in relation to molecular structure."

OBITUARY

The Council records with deep regret the deaths of Professor W. G. Duffield, Mr H. Chester Bell, Mr T. C. Lewis, Mr M. J. Jackson, Mr H. S. S. Harvey, Professor Sir L. Ray Lankester, Mr V. Lough, Dr H. Borns and Lt.-Col. J. W. Gifford.

MEMBERSHIP ROLL

The number of Honorary Fellows on the roll on December 31, 1930, was 11. At the same date ordinary Fellows numbered 754 and students 51.

The changes in the membership of the Society are shown in the appended table:

	Total Dec. 31, 1929	Changes during 1930			Total Dec. 31, 1930
Honorary Fellows	11				11
Ordinary Fellows	724	Elected		54	
		Student transfers		10	
				64	
		Deceased	15		
		Resigned or lapsed	19		
			—	34	
		Net increase		30	754
Students ...	51	Elected		12	
		Trans. to Fellow ...	10		
		Resigned	2		
			—	12	
		Net increase		0	51
Total membership	786	Net increase		30	816

REPORT OF THE TREASURER

The accounts for the year ended December 31st, 1930, show an adverse balance of £22. 2*s*. 10*d*.

This is largely due to the increase in the number of pages of the *Proceedings* published during the financial year. The publication, in conjunction with the Optical Society, of the discussion on "Photo-electric cells and their applications," was also a heavy expense, but it is hoped that the Society will more than recover this expenditure by sales.

The Society desires to thank the Council of the Royal Society for a grant of £200 towards the cost of publications.

The decrease in the amount charged to the Physical Society for *Science Abstracts* is due to the larger number of copies now taken by members of the Institution of Electrical Engineers.

£350 of 5 % War Loan was purchased in August at a cost of £364. 18*s*. 10*d*. The Society's investments have been valued at market prices on December 31st, 1930, through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank. Their value was approximately 7 % less at this date than on December 31st, 1929, owing to the continued depression of the stock market.

(Signed) ROBERT S. WHIPPLE
Honorary Treasurer

March 16*th*, 1931

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1930

1929 £ s. d.	EXPENDITURE	£ s. d.	£ s. d.
	To		
500 0 0	Stock of Publications at 1st January, 1930		600 0 0
647 0 0	"Science Abstracts"		566 0 0
	Ordinary Publications:		
1126 1 11	"Proceedings"	1374 12 10	
65 13 1	"Bulletin" and Notices	80 7 7	
56 6 3	General	72 19 6	
			1527 19 11
120 0 7	Postage on Publications		116 8 5
	Share of cost of printing and publishing "Photo-Electric Cells and their Applications"		378 10 2
72 17 1	Reporting at Meetings		66 4 7
34 13 5	Expenses at Meetings		33 11 2
610 15 8	Exhibition Expenses	744 10 2	
56 2 3	Optical Society Exhibition Account	52 17 9	
			797 7 11
6 4 7	Periodicals and Library		5 19 2
	Administration Expenses:		
178 18 8	Institute of Physics	169 11 8	
110 7 9	Office Expenses	112 18 9	
			282 10 5
	Printing List of Members		36 0 0
20 0 0	Guthrie Lecture (Honorarium)		20 0 0
28 15 4	Expenses incurred at Rugby Meeting		40 12 6
182 18 7	*Balance, being excess of Income over Expenditure, carried forward*		
£3816 15 2			£4471 4 3
	To Balance brought forward		£22 2 10

1929 £ s. d.	INCOME	£ s. d.	£ s. d.
	By		
600 0 0	Stock of Publications at 31st December, 1930		650 0 0
	Stock of "Photo-Electric Cells and their Applications"		129 0 0
	Subscriptions:		
1198 11 10	Fellows*	1242 1 3	
8 8 0	(Voluntary†)	8 3 0	
26 4 6	Students	28 17 6	
74 17 0	For "Science Abstracts" and Advance Proofs	102 4 0	
			1381 5 9
663 17 11	Sale of Publications		819 17 8
141 8 0	Advertisements in "Proceedings"		165 5 4
	Dividends from Investments and Bank Interest	245 1 5	
	Add: Income Tax refunded Jan.–April 4, 1930	16 17 11	
	Income Tax claimed April 5–Dec. 31, 1930	15 10 9	
		277 10 1	
250 14 11	*Less:* Transferred to Duddell Memorial Fund	20 0 0	
			257 10 1
673 17 8	Exhibitors' Payments on account of Exhibition		805 10 1
150 0 0	Royal Society Grant for Publications		200 0 0
28 15 1	Provincial Meeting (Rugby): Receipts from Sale of Railway and Coach Tickets		40 12 6
	Balance, being excess of Expenditure over Income, carried forward		22 2 10
£3816 15 2			£4471 4 3
	By Balance carried to Accumulated Fund		£22 2 10

* Eighty-seven Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate being £30. 5*s*. 9*d*.

† Voluntary subscriptions are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AT 31ST DECEMBER, 1930

LIABILITIES

	£	s.	d.	£	s.	d.	£	s.	d.
Accumulated Fund:									
As per last Balance Sheet				2161	19	7			
Entrance Fees, 1930				38	17	0			
				2200	16	7			
Less: Balance brought forward from Income and Expenditure Account	22	2	10						
Decreased value of Investments	282	18	10						
				305	1	8			
							1895	14	11
Life Compositions:									
As per last Balance Sheet				2321	0	0			
Received during year				63	0	0			
							2384	0	0
Duddell Memorial Trust Fund:									
As per last Balance Sheet				426	12	9			
Add Increased value of Investments				8	0	0			
							434	12	9
W. F. Stanley Trust Fund (For the "Bulletin"):									
As per last Balance Sheet				344	0	0			
Less Decreased value of Investments				79	0	0			
							265	0	0
A. W. Scott Bequest							250	0	0
Sundry Creditors							1801	15	0
Subscriptions paid in advance							59	12	10
							£7090	15	6

ASSETS

	£	s.	d.	£	s.	d.
Investments at Market Value on date:						
£600 Consolidated Stock 2½ %	336	0	0			
£1000 War Loan 5 % 1929/47 Inscribed "A" Account	1020	0	0			
£400 War Loan 5 % 1929/47 Inscribed "B" Account	408	0	0			
£650 Funding Loan 4 % 1960/90	579	0	0			
£500 India 3½ % Stock	280	0	0			
£254. 2*s.* 9*d.* New South Wales 5 % Stock 1935/55	128	0	0			
£211 London County Consolidated 4½ % Stock	206	0	0			
£400 Lancaster Corporation 3 % Redeemable Stock	268	0	0			
£399 London Midland and Scottish Railway 4 % Debenture Stock	292	0	0			
£1000 London Midland and Scottish Railway 4 % Preference Stock	510	0	0			
£500 London and North Eastern Railway 4 % Debenture Stock	355	0	0			
£150 Southern Railway 5 % Debenture Stock	144	0	0			
£300 Southern Railway Preferred Ordinary Stock	180	0	0			
£442 Southern Railway Deferred Ordinary Stock	85	0	0			
				4791	0	0
Stock of Publications (as per Treasurer's Valuation)				779	0	0
Subscriptions due				32	8	6
Sundry Debtors				75	11	0
Inland Revenue—Income Tax reclaimed for 1930				15	10	9
Cash at Bank:						
On Deposit Account	1200	0	0			
On Current Account	172	6	10			
Cash in hand	24	18	5			
				1397	5	3
				£7090	15	6

ROBERT S. WHIPPLE, *Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balances and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

SPENCER HOUSE, E.C. 2
16th March 1931.

KNOX, CROPPER & CO.,
Chartered Accountants

Examined and approved on behalf of the Society (Signed) E. H. RAYNER.
(Signed) W. S. TUCKER.

LIFE COMPOSITION FUND AT DECEMBER 31ST, 1930

	£	s.	d.
128 Fellows paid £10	1280	0	0
3 Fellows paid £15	45	0	0
1 Fellow paid £20	20	0	0
1 Fellow paid £20. 10*s*.	20	10	0
14 Fellows paid £21	294	0	0
23 Fellows paid £31. 10*s*.	724	10	0
	£2384	0	0

W. F. STANLEY TRUST FUND (FOR THE "BULLETIN")

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	180	0	0	Carried to Balance Sheet	265	0	0
£442 Southern Railway Deferred Ordinary Stock	85	0	0				
	£265	0	0		£265	0	0

DUDDELL MEMORIAL TRUST FUND

CAPITAL

	£	s.	d.		£	s.	d.
£400 War Loan 5 % 1929/47 Inscribed Stock	408	0	0	Carried to Balance Sheet	408	0	0

REVENUE

	£	s.	d.		£	s.	d.
Balance at 31st December, 1929	26	12	9	Honorarium to Medallist	20	0	0
Dividends	20	0	0	Balance carried to Balance Sheet	26	12	9
	£46	12	9		£46	12	9

AN IMPORTANT NEW BOOK

A SURVEY OF
PHYSICS

by

F. A. SAUNDERS

Professor of Physics, Harvard University

In a single volume Prof. Saunders gives not only a survey of all the general physics demanded, for example, by a pass degree examination, but also concise accounts of recent technical applications and of the fundamental theoretical and experimental advances of the last few years, with copious illustrations. This book fills ideally the gap which has existed for so long between the popular exposition and the advanced text-book demanding specialized mathematical and physical knowledge. It will be invaluable for the teacher who has to arrange a course in physics which will interest his hearers, and will be enjoyed by every reader who wants to know what modern physics is doing.

Many diagrams & illustrations, 14s. net

[LONDON: G. BELL & SONS, LTD.]

PITMAN'S BOOKS

A New and Enlarged Edition of

TELEVISION
TO-DAY AND TO-MORROW

By SYDNEY A. MOSELEY and H. J. BARTON CHAPPLE, Wh.Sc., B.Sc. (Hons.), A.C.G.I., D.I.C., A M.I.E.E.

Foreword by JOHN L. BAIRD

This extremely popular and authentic account of the discovery, development and possibilities of television has been carefully revised and brought completely up-to-date. A new chapter on latest developments has been added and the number of illustrations considerably increased. The purely scientific aspects of the subject are clearly and interestingly dealt with and every reader will gain a sound technical idea of the principles underlying this important invention.

CONTENTS (Abbrev.). History of Television—The General Details—The Baird Transmitter—The Baird "Televisor" Receiver—Synchronism in Television—Photo-electric Cells and Neons—The Wireless Receiver for Television—Tele-Cinema and Tele-Talkies—Noctovision and the "Noctovisor" Receiver—Daylight Television—Colour and Stereoscopic Television—New Developments—Television in Other Countries.

NOW READY 7/6 NET NOW READY

PHOTOELECTRIC CELLS.

By Dr NORMAN CAMPBELL and DOROTHY RITCHIE. Cloth gilt, 216 pp., with numerous illustrations. Second edition. 15s. net.

"The book is certainly remarkable in the manner in which it conveys detailed and advanced information with the assistance of a minimum of mathematics."
(*Proceedings of Physical Society*)

RADIOACTIVITY AND RADIOACTIVE SUBSTANCES.

By J. CHADWICK, M.Sc. With a Foreword by Sir ERNEST RUTHERFORD, Bart. Cloth, with many diagrams and illustrations. Third edition. 2s. 6d. net.

"It can safely be said that the book is the best introductory treatise of its size existent."
(*Proceedings of Physical Society*)

ALTERNATING CURRENT BRIDGE METHODS.

By B. HAGUE, D.Sc., D.I.C., etc. Cloth gilt, demy 8vo, with 112 illustrations. Second edition, revised. 15s. net.

"This is an excellent book....No one who has to deal with a bridge can afford to be without this book."
(*Journal of Scientific Instruments*)

Descriptive leaflets of the above, post free on request

SIR ISAAC PITMAN & SONS, LTD., Parker Street, Kingsway, London, W.C. 2

PUBLICATIONS OF THE PHYSICAL SOCIETY

PROCEEDINGS

Vol.		
1	(3 pts)	12*s.* each.
2	(5 „)	12*s.* each.
3	(4 „)	12*s.* each.
4	(5 „)	Pts 1, 2, 3 and 5, 7*s.* each. Pt 4, 12*s.*
5	(5 „)	7*s.* each.
6	(4 „)	Pt 1, 12*s.* Pts 2, 3 and 4, 7*s.* each.
7	(4 „)	7*s.* each, except pt 1, 12*s.*
8	(4 „)	7*s.* each.
9	(4 „)	7*s.* each.
10	(4 „)	7*s.* each.
11	(4 „)	Pt 1, 7*s.* Pts 2, 3 and 4, 12*s.* each.
12	(4 „)	Pt 1, 12*s.* Pts 2, 3 and 4, 7*s.* each.
13	(13 „)	7*s.* each, except pt 12, 12*s.*
14	(12 „)	7*s.* each, except pt 12, 12*s.*
15	(12 „)	7*s.* each.
16	(8 „)	7*s.* each.
17	(7 „)	7*s.* each.
18	(7 „)	7*s.* each.
19	(8 „)	7*s.* each.
20	(6 „)	7*s.* each.
21	(7 „)	7*s.* each.
22	(4 pts)	7*s.* each, except pt 2, 12*s.*
23	(5 „)	Pts 1, 3, 4 and 5, 7*s.* each. Pt 2, 12*s.*
24	(6 „)	7*s.* each, except pt 1, 12*s.*
25	(5 „)	7*s.* each.
26	(5 „)	7*s.* each.
27	(5 „)	7*s.* each.
28	(5 „)	7*s.* each.
29	(5 „)	7*s.* each.
30	(5 „)	7*s.* each, except pt 5, 12*s.*
31	(5 „)	Pts 1, 2, 3 and 4, 7*s.* each. Pt 5, 12*s.*
32	(5 „)	12*s.* each.
33	(5 „)	7*s.* each.
34	(5 „)	Pts 1, 3, 4 and 5, 7*s.* each. Pt 2, 12*s.*
35	(5 „)	7*s.* each.
36	(5 „)	7*s.* each.
37	(5 „)	7*s.* each.
38	(5 „)	Pts 2, 3, 4 and 5, 7*s.* each. Pt 1, 12*s.*
39	(5 „)	7*s.* each.
40	(5 „)	7*s.* each.
41	(5 „)	7*s.* each.
42	(5 „)	7*s.* each.

Postage is charged extra. The sale of Parts the price of which is 12*s.* is restricted, and permission to purchase them must be obtained from the Council of the Society.

The Proceedings can be supplied in bound volumes at an additional charge of 5*s.* per volume.

SOME SPECIAL PUBLICATIONS

The Teaching of Geometrical Optics. Price 4*s.* 6*d.*

Report on Series in Line Spectra. By *A. Fowler*, F.R.S. Second Edition, with index. Price 12*s.* 6*d.*; in cloth, 15*s.* 6*d.*

Report on Radiation and the Quantum Theory. By *J. H. Jeans*, F.R.S. Second Edition. Price 7*s.* 6*d.*; in cloth, 10*s.* 6*d.*

Report on the Relativity Theory of Gravitation. By *A. S. Eddington*, F.R.S. Third Edition. Price 6*s.*; in cloth, 8*s.* 6*d.*

The Effect of Electric and Magnetic Fields on Spectral Lines (Seventh Guthrie Lecture). By *Niels Bohr*. Price 2*s.* 6*d.*

The Scientific Papers of James Prescott Joule. In cloth. Vol. I, 18*s.*; Vol. II (Joint Papers), 12*s.*

The Scientific Papers of Sir Charles Wheatstone. In cloth. Price 12*s.*

Discussions. Photo-Electric Cells and their Applications, 12*s.* 6*d.*; The Making of Reflecting Surfaces, 5*s.*; Lubrication, 1*s.* 6*d.*; Ionisation in the Atmosphere, 3*s.*; Hygrometry, 5*s.*; Metrology in the Industries, 1*s.* 6*d.*; Absolute Measurement of Electrical Resistance, 2*s.* 6*d.*; X-Ray Measurements, 2*s.* 6*d.*; Physics and Chemistry of Colloids, 2*s.* 6*d.*

Postage is charged extra.

Fellows of the Society may obtain any of the above publications for their PERSONAL *use at* HALF-PRICE. *An additional charge is made for binding.*

Orders for any of the above publications should be sent to the

Assistant Secretary, The Physical Society, 1 Lowther Gardens,
Exhibition Road, London, S.W. 7

from whom a full list of the Society's publications may be obtained.

PRINTED IN GREAT BRITAIN BY W. LEWIS, M.A., AT THE CAMBRIDGE UNIVERSITY PRESS